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U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP804

Part of Journal of Research of the National Bureau of Standards, Volume 15, July 1935

BRIGHTNESS METER FOR SELF-LUMINOUS DIALS

By Leon F. Curtiss

ABSTRACT

A compact, self-contained apparatus is described which can be used to determine the brightness in microlamberts of a self-luminous dial. The arrangement consists of a translucent-glass disk uniformly illuminated from the back by a flashlight bulb. An opaque stencil, cut to match the figures on the dial to be tested, is fitted to the front of the disk. The intensity of illumination and, therefore, the brightness of the face of the glass disk is controlled by a wheatstone-bridge arrangement which regulates the current through the bulb, supplied by two flashlight dry cells. A milliammeter is connected to show the out-of-balance current of the wheatstone bridge and may be calibrated directly in microlamberts. The range of the apparatus is from 1 to 50 microlamberts, which upper limit exceeds the brightness of any commercial dials now made. The device is easily portable and can be used to test dials mounted in instrument panels without dismounting them.

I. INTRODUCTION

There is a demand at the present time on the part of users and makers of self-luminous dials for some form of photometric device which can be used to test the brightness of completed dials, both immediately after manufacture or purchase and at intervals during their serviceable life. Two methods which have been followed in the past for this purpose, are somewhat unsatisfactory. One is the use of a portable photometer in which the brightness is varied by changing the distance between a calibrated lamp and a diffusing screen over which is fitted an opaque stencil pierced with figures to match the dial under test. This photometer is bulky and not very easily portable. In particular, it is not at all adapted to testing dials already installed, unless they are dismounted for purposes of test.

The second method is to prepare a self-luminous screen made by mounting a layer of luminous powder between two sheets of glass. This is fitted with an opaque stencil to match the dial to be tested. Although this arrangement is readily portable, it merely permits the observer to determine whether the dial is brighter or dimmer than the standard. Furthermore, such standards of brightness are subject to the steady deterioration of all self-luminous compounds.

The writer has approached the problem with the point of view of providing a very compact photometer in which the brightness is

controlled by varying the current through the lamp at a fixed distance from the diffusing screen. In working out such an arrangement, he has followed the design as suggested by B. H. Crawford [1] in which the variation of brightness is produced by changing the current through a lamp placed in one arm of a wheatstone-bridge circuit. A milliammeter is connected to read the out-of-balance current produced by changes in the resistance of the lamp as the applied voltage is changed. This paper describes an instrument built on this principle, adapting an arrangement described previously [2] for measurement of luminous powder in the dry state to the measurement of completed dials.

II. DESCRIPTION OF INSTRUMENT

Figure 1 shows the luminous disk in elevation, and a cross-section view of the luminous disk which is used to obtain a comparison of brightness with the self-luminous dials. The disk is made up of two pieces of opal glass O, clamped to each side of a green-glass disk G, which is cut from a Corning green railway-signal roundel having a transmission of approximately 140 percent on the American Railway Scale. The opal-glass disks are each about ⅛ inch thick. Back of these glasses a flat-white diffusing reflector D is mounted. The shape of this reflector is not very important. A hemispherical surface would do very well. However, such a shape would make the depth of the cell greater than is desirable. The nature of the surface is, however, quite important. The best surface is obtained by "smoking" with burning magnesium. Care must be taken to prevent any contact with this surface after it has been prepared. A 3-cell flashlight bulb F projects through a hole in the center of the reflector D. This bulb is fitted with an opaque cap C. In this way practically uniform illumination is obtained over the whole of the glass disk, although the cell is only 2 inches deep, as indicated by the scale at the bottom of the drawing.

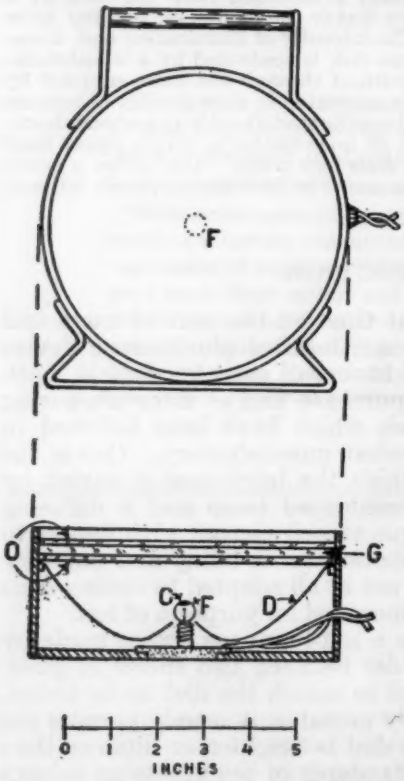

FIGURE 1.—*Luminous disk in elevation and cross section.*

The wheatstone-bridge resistors, rheostats, battery, and meter are contained in a separate small aluminum box with bakelite cover, shown in the drawing in figure 2. This box is connected with a flexible 2-wire cable to the flashlight bulb shown at F in figure 1. The wiring diagram of the complete arrangement is shown in figure 3.

[1] J. Sci. Instr., 11, 14 (1934).

[2] J. Research NBS 13, 203 (1934) RP702.

The values of the resistances of the various arms of the bridge are indicated. The voltage applied to the bulb, supplied by 2 flashlight cells, is controlled by the radio-type rheostats R_1 and R_2. The one of lower resistance is used when a fine adjustment of brightness is desired. Since the flashlight bulb is always operated well below its rated voltage, it can be expected to give long service with a fairly stable calibration. Unless subjected to abuse, this instrument should require recalibration only at very infrequent intervals. The milliammeter M, having a full-scale deflection of 1.5 milliamperes, is connected as shown to measure the out-of-balance current of the bridge. Its readings are, therefore, approximately proportional to the brightness of the lamp. The exact relation is of no importance since it is simpler to calibrate each instrument separately. The instrument is calibrated by observing the brightness of the luminous disk, by comparison with that of a screen of known transmission illuminated by a standard lamp, at various readings of the milliammeter. In this way the scale of the meter may be graduated directly in microlamberts.

The actual values of the resistances may vary slightly in different instruments since careful adjustment of at least one of the arms of the wheatstone bridge is required to bring the out-of-balance currents of the wheatstone bridge within the range of the milliammeter selected.

The values given in figure 3 should be convenient for making the necessary preliminary adjustments.

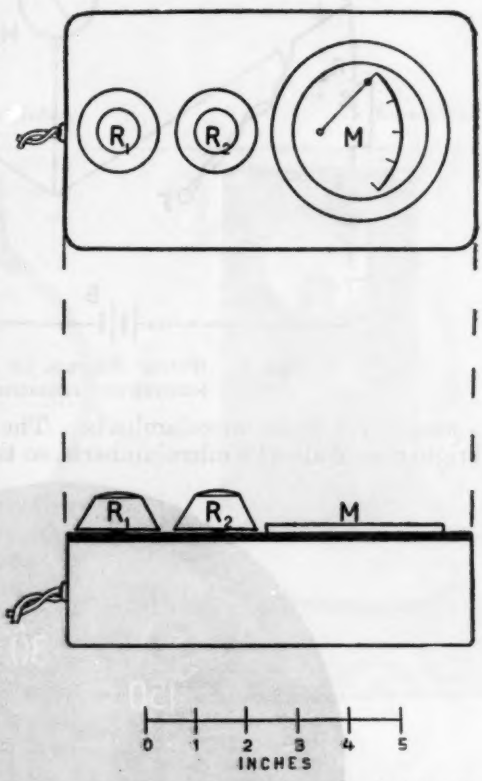

FIGURE 2.—*Top and side view of control box for luminous disk.*

To complete the instrument, a stencil cut from opaque material with characters to match those on the dial is required. This stencil is clamped to the front of the luminous disk. Such a stencil is shown in figure 4. In making measurements, the luminous disk with stencil is placed beside the dial to be tested and the brightness varied until a match is obtained. This method gives sufficient accuracy for all practical purposes. Measurements on unmounted dials may be made with the comparison dial resting on the base provided to hold it in an upright position. However, this part of the apparatus is thin and light enough so that it may be held near a dial mounted in an instrument panel so that a measurement can be obtained without removing the dial.

A photograph of a completed instrument is shown in figure 5. The total weight is about 6 pounds. As described, this instrument has

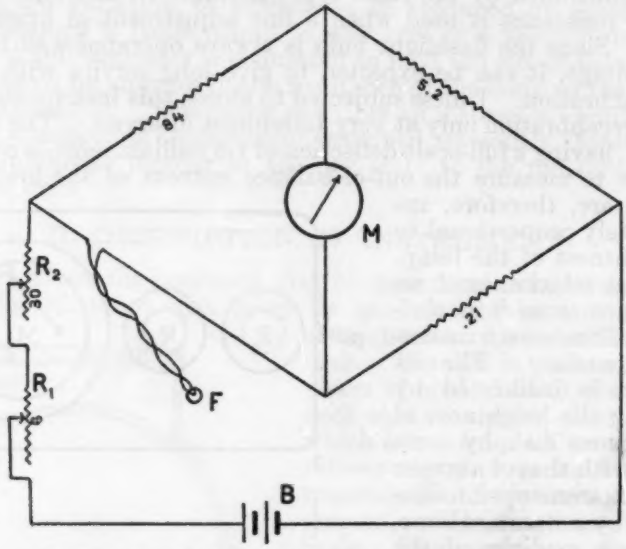

FIGURE 3.—*Wiring diagram for the brightness meter.*
Numerals show resistances in ohms.

a range of 1 to 50 microlamberts. The average luminous dial has a brightness of about 6 microlamberts, so this range is entirely adequate.

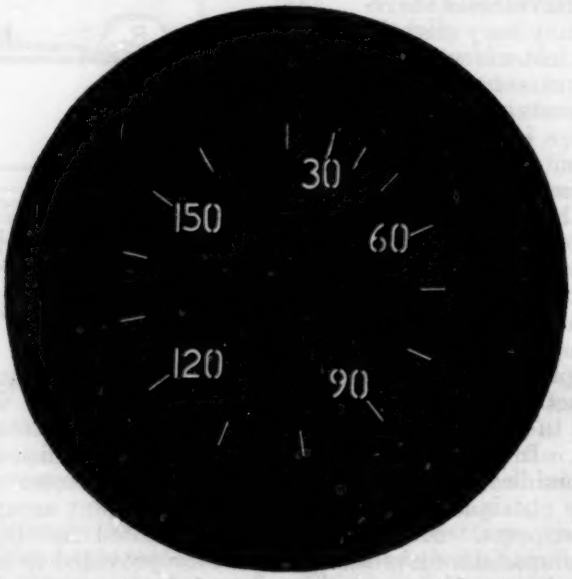

FIGURE 4.—*Opaque stencil used to form artificial dial.*

The writer wishes to thank B. W. Brown and Miss C. L. Torrey for help in designing the instrument.

WASHINGTON, May 7, 1935.

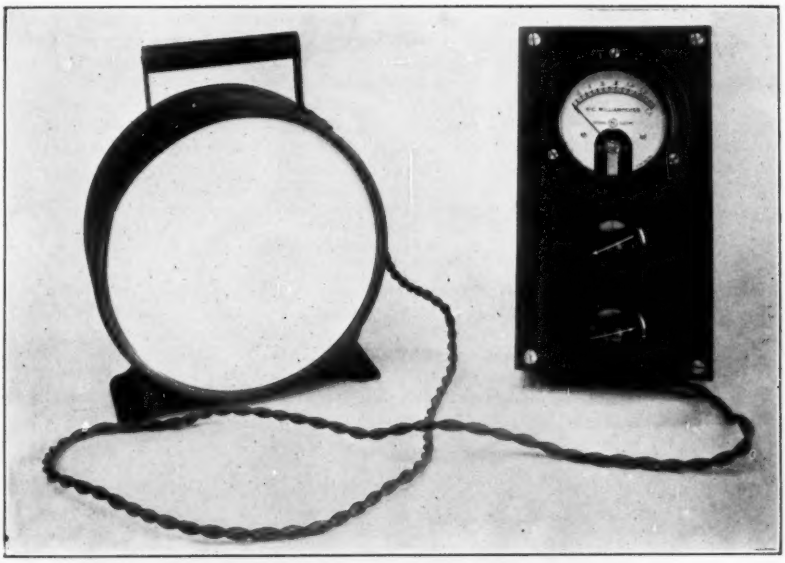

FIGURE 5.—*Completed brightness meter.*

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP805

Part of Journal of Research of the National Bureau of Standards, Volume 15, July 1935

METHOD FOR MEASURING THE pH OF LEATHER USING A SIMPLE GLASS-ELECTRODE ASSEMBLY

By Everett L. Wallace

ABSTRACT

The glass electrode has been shown to function under conditions which are not favorable to either the hydrogen or quinhydrone electrode. Glass electrodes are now available which may be used in place of the hydrogen electrode, in the conventional potentiometric system, by substituting a galvanometer of high sensitivity and suitable characteristics in the electrical circuit. In view of the general use of pH measurements in specification and control work in the leather industry, a method which is rapid and accurate is desirable. A study has therefore been made of a simple glass-electrode assembly for measuring the pH value of leather extracts and tannin solutions. A method is proposed and the details of operation noted which are essential for accurate routine pH measurements. The Kerridge method of converting the emf readings of the glass electrode to corresponding pH units is described.

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I. INTRODUCTION

Kohn and Creede,[1] in 1923, suggested making pH measurements of water solutions in equilibrium with finely divided leather and plotting neutralization curves for a sufficient number of leathers of known tannage and wearing quality so as to establish a permissible upper limit for acidity. All the leathers which they considered good had an initial pH of practically 3 or higher. Since that time many other workers [2] have devised methods which involve the measurement of the pH of leather-water systems.

While interest in the possibility of using pH as a means of evaluating leather with respect to acidity has been increasing, the practical application of the method has made slow progress. The chief reason for this has been lack of confirmatory experimental data, correlating pH and the deterioration of leather as influenced by acid content, the kind of tanning materials used, and storage conditions.

Results of research are now available,[3] however, which show the correlation between the initial pH values of different leathers and their

[1] J. Am. Leather Chem. Assn, 18, 189 (1923).
[2] See BS J. Research 10, 560 (1933) RP547 for list of references.
[3] J. Am. Leather Chem. Assn. 28, 125 (1933); 29, 623 (1934); 30, 91 (1935).

deterioration in storage. These data serve as a valuable guide in selecting safe pH limits for vegetable-tanned leather.

The increased knowledge of the significance of the pH of leather will logically lead to its greater use in specifications and control work. This necessarily requires that the method for measuring pH be standardized. Equipment for this purpose has generally included the hydrogen electrode or in some cases the quinhydrone electrode. The latter has been shown to give erratic results in solutions containing tannin.[4] The hydrogen electrode is susceptible to poisoning by many of the materials present in leather, and usually not more than two or three reliable readings can be obtained without renewing the coating on the platinum foil. The glass electrode has been shown [5] to function satisfactorily with leather extracts and other solutions under conditions unfavorable to the use of either the hydrogen or the quinhydrone electrode or of indicators. Recently glass bulbs of low resistance have been made available, which may be used in the conventional potentiometric systems by substituting a galvanometer of high sensitivity and suitable characteristics in the electrical circuit. This development offers an assembly for use in making pH measurements which gives rapid and reliable results.

This report describes the glass-electrode assembly used, the essential details of operation which were followed, and the experimental work incident to the development of a method for measuring the pH of leather and tannin extracts.

II. EQUIPMENT

The apparatus used in this study is shown in figure 1. The potentiometer is a portable type calibrated to ± 0.5 millivolt. The galvanometer has a sensitivity of 0.0005 microampere, a 6-second period and a critical-damping resistance of 10,000 ohms. The reference half cell is a saturated potassium-chloride-calomel electrode, with side arm for dipping into the test solution and a dropping funnel inserted in the top for flushing after each determination. The half cell was placed in a dewar flask for protection against sudden changes of temperature. The glass electrode is of the bulb type having an internal reference electrode.

The glass electrode was insulated by supporting it from a bakelite rod. Shielding and grounding were found necessary, particularly during humid weather. The wires leading to the galvanometer were shielded with grounded metal cables and the galvanometer was shielded by a grounded copper case. The potentiometer rested on a grounded copper shield. Where possible the reading lamp should be lighted by alternating current, using a small transformer, since the use of direct current often causes induced currents which may affect the stability of the galvanometer coil.

III. STANDARDIZATION

Two glass electrodes having similar internal reference cells will not necessarily give the same emf readings in a standard buffer solution. This is caused by a difference in potential between the inner and outer surfaces of the glass, known as the "asymmetry potential" of the glass membrane.

[4] BS J. Research **4**, 737 (1930) RP176.
[5] Burton and Acree, Ind. Eng. Chem. **6**, 79 (1934).

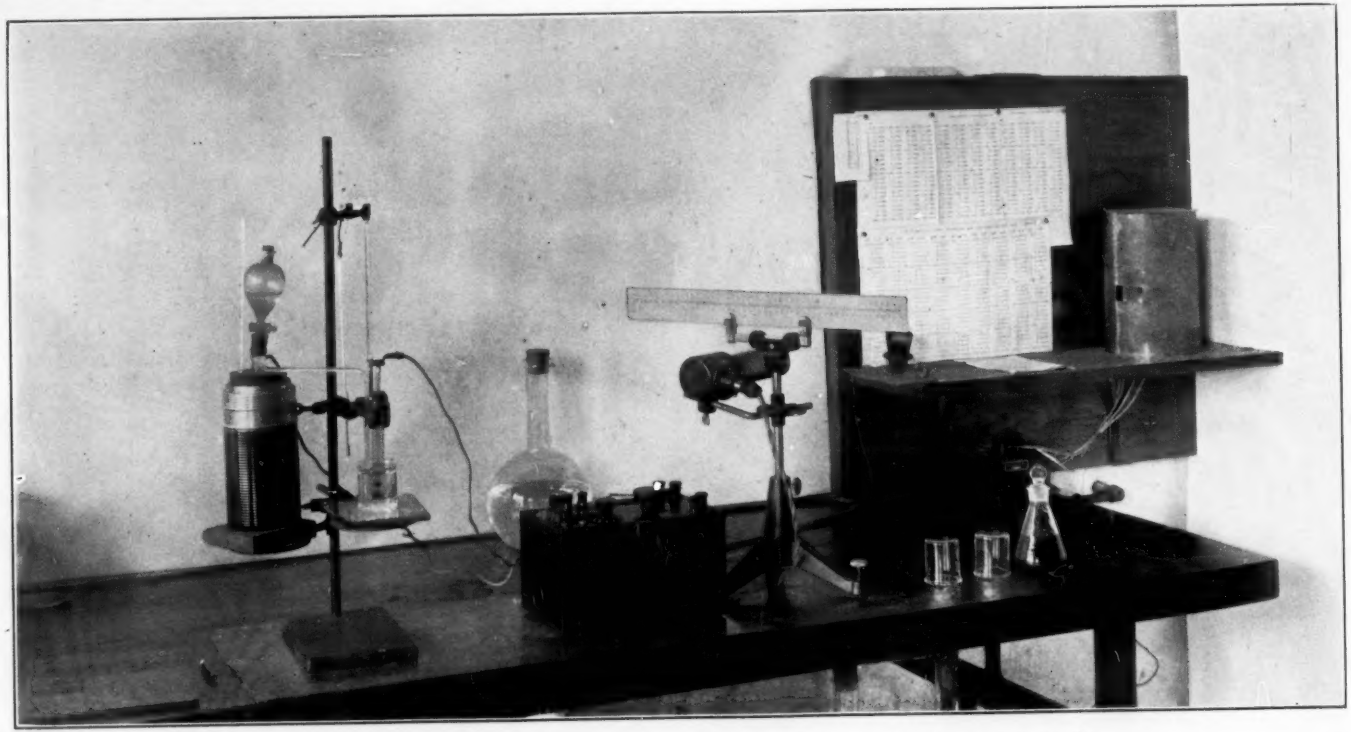

FIGURE 1.—*Apparatus used for making* pH *measurements with the glass electrode.*

This potential is not constant, but the change is usually very gradual over a period of weeks. Different electrodes may have slightly different characteristics, and for this reason the glass electrode should be considered as a secondary electrode which must be calibrated against the standard hydrogen electrode.

Since the glass electrode must be frequently calibrated, prepared tables for converting emf readings into corresponding pH units can be used only after a correction factor has been applied.

When the observed emf of a glass electrode is plotted graphically against the known pH of several buffer solutions, a straight-line graph, figure 2, should be obtained. This line will have a slope of 0.0591 volt per pH unit at 25° C within the range of 1 to 10 pH. Therefore,

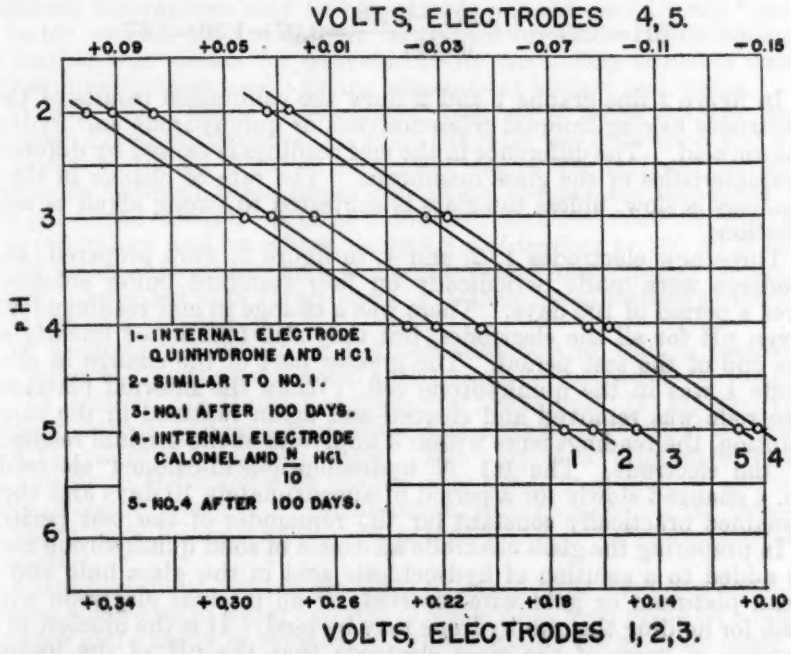

FIGURE 2.—*Calibration graphs for glass electrodes with four buffers, versus saturated potassium-chloride-calomel electrode at 25° C.*

for routine work it is usually sufficient to check the electrode against a standard buffer solution, having a pH near the working range desired.

The following formula for converting emf readings into corresponding pH units, described by Kerridge,[6] is simple, eliminates any necessity for separate computation of the corrections in the readings, and applies to any internal reference cell.

$$pH_x = pH_b + \frac{E_b - E_x}{K},$$

where x = the unknown solution, b = the standard buffer solution used for calibration, and $K = (0.00019832)\ (273.1 + t)$, where t = tem-

[6] J. Sci. Instr., 3 404 (1926).

perature in degrees C. The equation is given in algebraic form and emf readings must be inserted with proper signs. The sign given the glass electrode in this report is taken as the sign [7] on the outer metallic terminal of the electrode, and is the same as that of the potentiometer binding post to which the glass electrode is attached at balance. This is the convention accepted by the National Bureau of Standards.

The following calculation is typical. If the observed emf reading at 25° C of a buffer solution (pH 3.97) with the glass electrode *versus* the saturated potassium-chloride-calomel electrode was found to be +0.221 volt and the observed emf of an unknown solution was +0.298 volt, then:

$$\text{pH}=3.97+\frac{+0.221-0.298}{0.0591}=3.97-1.30=2.67$$

In figure 2 line graphs 1 and 2 show the calibration results of two electrodes having internal reference cells of quinhydrone and hydrochloric acid. The difference in the emf readings is caused by different characteristics of the glass membrane. The rate of change in these readings is slow, unless the glass is subjected to strong alkali or acid solutions.

Three new electrodes 1, 2, and 4, in figure 2, were prepared, and readings were made periodically on four standard buffer solutions over a period of 100 days. There was a change in emf readings for a given pH for all the electrodes, but they still functioned linearly at the end of the test period. The greater part of the change in electrode 1 was in the quinhydrone cell. When the internal platinum electrode was removed and cleaned and again replaced in the same solution, the readings were within 3 millivolts of the original readings of the electrode. The 0.1 *N* hydrochloric-acid-calomel electrode no. 4 changed slowly for a period of approximately 10 days and then remained practically constant for the remainder of the test period.

In preparing the glass electrode an excess of solid quinhydrone may be added to a solution of hydrochloric acid in the glass bulb and a clean platinum or gold wire inserted, or an internal electrode with bulb for holding the quinhydrone may be used. It is the opinion of a number of users of the glass electrode that the pH of the hydrochloric-acid solution used with the quinhydrone must be exactly 1, in order that tables furnished with some electrodes may be used for converting emf readings into pH units. This is not the case, since the emf of the glass electrode is practically independent of the pH of the hydrochloric-acid solution. This condition is caused by the fact that the potentials of the glass and quinhydrone electrodes are changed the same amount, whenever the pH of the internal hydrochloric-acid solution is changed. Any concentration of hydrochloric acid between normal and 0.1 normal is satisfactory for routine work.

In preparing a calomel internal reference electrode it must be provided with a bulb for holding the mercury and calomel in contact with the platinum wire. The emf of the glass electrode with an internal calomel electrode will vary with change in the pH of the internal hydrochloric-acid solution, because the glass acts as a hydrogen

[7] Trans. Am. Electrochem. Soc. 36 3 (1919).

electrode while the mercury acts as a metal electrode. The solution usually used is 0.1 *N* hydrochloric acid.

The proper correction should be made in the conversion formula for the temperature at which the pH determinations are made with the glass electrode. The temperature of the solutions measured should be near that of the calomel reference electrode. A difference of 5° C will cause an error of approximately 0.06 pH unit.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Since the method for measuring the pH of leather is empirical and is dependent upon the dilution of the extract (ratio of leather to water), it is necessary to establish a standard method, in order that work of different laboratories may be comparable. Kohn and Creede [8] used a factor weight, 4.9 g of leather to 100 ml of water. This amount of leather was chosen for convenience in calculating titration data. Other investigators used varying amounts of leather and water.

It was found from experimental data on a large number and variety of leather samples that, when the ratio was between 4 and 6 g of leather to 100 ml of water, the extract was so well buffered that any variation between these limits caused no appreciable difference in the pH of the extract. A large amount of data had been collected in this laboratory and by others, using 4.9 g of leather to 100 ml of distilled water. In order that the accumulated data might be more closely correlated with future work, a ratio of 5 g of leather to 100 ml of water was selected.

In a committee report on the determination of acid in leather,[9] the following items were studied with respect to their effect on the pH of the leather: (1) Method of preparing the sample; (2) filtering the leather extract; (3) grease content of the sample; (4) time of soaking, and (5) ratio of leather to water. The only factors found to have any appreciable influence on the pH were the time of soaking and the ratio of leather to water. The minimum time required for the sample to reach equilibrium with the water was found to be approximately 4 hours.

A comparison of the pH readings obtained with the glass and hydrogen electrodes in water extracts of leather has been made on a large number and variety of samples. Typical results are given in table 1, in which the pH values of 24 samples representing commercial and specially treated leathers measured with the hydrogen and glass electrodes, are shown.

TABLE 1.—pH *measurements with glass and hydrogen electrodes in water extracts of leather*

Sample	Glass	Hydrogen	Sample	Glass	Hydrogen	Sample	Glass	Hydrogen
1	5.25	5.08	9	2.75	2.74	17	4.64	4.61
2	2.66	2.66	10	2.73	2.76	18	3.03	3.04
3	3.57	3.47	11	2.76	2.76	19	2.54	2.50
4	2.28	2.25	12	2.75	2.72	20	3.97	3.97
5	3.19	3.21	13	2.76	2.77	21	4.50	4.50
6	3.19	3.18	14	3.19	3.21	22	2.48	2.49
7	3.19	3.18	15	3.34	3.35	23	2.64	2.67
8	2.75	2.74	16	2.97	2.98	24	3.59	3.54

[8] J. Am. Leather Chem. Assn. **18**, 189 (1923).
[9] J. Am. Leather Chem. Assn. **29**, 403 (1934).

It will be noted that the agreement was close with two exceptions. In sample 1 the hydrogen electrode was "poisoned" so rapidly that a steady reading could not be made, and in sample 3 copper plated out of the solution onto the hydrogen electrode.

In order to determine the effect of the tannins on the pH of leather, the pH-titration curves shown in figure 3 were made with the glass electrode in a sulphuric-acid solution and in solutions of sulphuric acid of the same strength containing commercial tannin extract. In the pH range between 3 and 4, where it has been shown that leather is unharmed by the acidity, the type or amount of tannin has little effect on the pH. Above pH 4 there is a large difference in the buffering effects of quebracho and chestnut tannin extracts. This indicates that the water-soluble tannins extracted from the leather

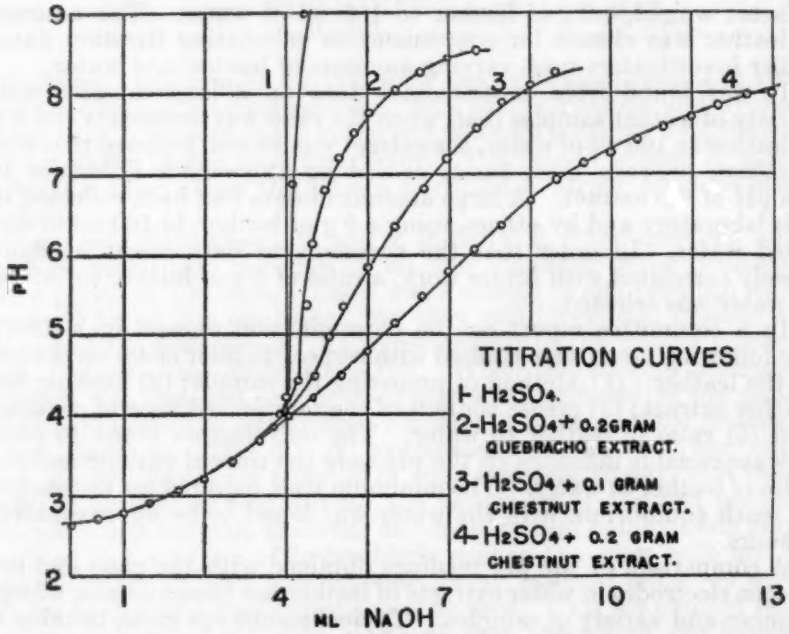

FIGURE 3.—*Titration curves for sulphuric-acid solution and for sulphuric-acid solutions of the same strength containing tannin.*

have no effect on the acidity within the normal range of a routine pH determination.

The effect of the temperature of the water used for extracting the leather, on the pH of the extract was determined as follows. Two leathers were used. One was tanned in the laboratory and treated with sulphuric acid and the other was a commercial sole leather. Distilled water (100 ml) at 25° C was added to 5-g portions of the leathers, as prepared for analysis, in glass-stoppered flasks.

One series was allowed to come to equilibrium at 10° C, one at 45° C, and the other maintained at 25° C. After 24 hours the solutions were filtered and pH determinations made at 25° C. The maximum variation in the samples was only 0.03 pH.

V. SUMMARY

1. From the results of this work it is recommended that the procedure for determining the pH value of leather proposed in the report of the committee on the determination of acid in leather [10] be revised to permit only the use of the glass electrode. The method should read as follows: Weigh 5 g of leather, as prepared for analysis, into a flask, add 100 ml of distilled water and stopper the flask tightly. Agitate the mixture immediately and allow it to stand for 4 hours. Again agitate the mixture and allow it to settle for 10 minutes, and determine the pH of the decanted extract with the glass electrode.

2. The glass electrode was found to be more rapid and to require less attention than the hydrogen electrode.

3. The Kerridge substitution method of converting emf readings of the glass electrode into corresponding pH units is described.

WASHINGTON, May 10, 1935.

[10] J. Am. Leather Chem. Assn. **29**, 403 (1934).

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP806

Part of Journal of Research of the National Bureau of Standards, Volume 15, July 1935

EFFECT OF PRESSURE ON THE DIELECTRIC CONSTANT, POWER FACTOR, AND CONDUCTIVITY OF RUBBER-SULPHUR COMPOUNDS [1]

By Arnold H. Scott

ABSTRACT

The dielectric constant, power factor, and conductivity of rubber-sulphur compounds containing from 0 to 32 percent of sulphur were measured while subjected to pressures ranging from 1 to 700 bars (approximately 690 atmospheres). The dielectric constant and power factor were measured at 1,000 cycles per second and the conductivity at the end of 1-minute electrification. The effect of pressure on each of the electrical properties was found to change with sulphur content. The dielectric constant of specimens containing up to about 7.5 percent of sulphur increased slightly with pressure. For higher percentages of sulphur it decreased with pressure. The power factor of specimens containing up to about 2 percent of sulphur was independent of the pressure. For percentages of sulphur from 2 to about 12 percent, the power factor increased with pressure; for higher percentages of sulphur it decreased with pressure. The conductivity of specimens containing between about 12 and 19 percent of sulphur increased with pressure, while it decreased with pressure for other percentages of sulphur. Curves are presented which show the effect of pressure on these electrical properties for rubber-sulphur compounds of any possible composition.

The effect of pressure on the electrical properties of two specimens of gutta-percha over the same pressure range was determined and the results are given for comparison.

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[1] This paper includes the subject matter used in a dissertation submitted to the board of university studies of The Johns Hopkins University in partial fulfillment of the requirements for a degree of doctor of philosophy. A copy of this dissertation is on file at the library of the university.

I. INTRODUCTION

This paper reports the results of a study on the effect of pressure on the dielectric constant, power factor, and conductivity of rubber-sulphur compounds, and is the third paper of a series dealing with the electrical properties of rubber-sulphur compounds.[2] The previous papers dealt with the effect of sulphur content, temperature, and current frequency on these electrical properties. The results reported in the present paper have been corrected for changes in the dimensions of specimens caused by changes in pressure. The required data for making these corrections were obtained from a detailed study of the compressibility of rubber-sulphur compounds which has recently been completed.[3]

II. METHOD OF DETERMINING ELECTRICAL PROPERTIES

The specimens were made in the form of insulation on wires in order that they might be put in a pressure apparatus consisting of heavy pipes. Each material under test was formed into an insulating cylinder around the wire. The specimen was placed in the pressure apparatus in such a way that the wire core was used as one electrode and the pressure medium as the other. This made a cylindrical capacitor having the material under test as the dielectric. The capacitance, power factor, and conductance of this capacitor were measured when the various pressures were applied.

The dielectric constant, K, of a material is given by the equation

$$K=AC \tag{1}$$

where C is the capacitance of the capacitor having this material as the dielectric, and A is the shape factor of the capacitor. For certain shapes of the capacitor, A may be readily computed from easily determined dimensions and the dielectric constant obtained from a measurement of the capacitance. However, the specimens used in this investigation were not sufficiently uniform and symmetrical to permit the computation of A. Therefore, an indirect method was used in the determination of A. The dielectric constant of the material was determined by means of flat specimens at atmospheric pressure and 25° C as described by Curtis, McPherson, and Scott.[4] The flat specimen for this purpose usually was made at the same time and from the same batch of material as the cylindrical specimen. The value of A for the cylindrical specimen could then be computed from the capacitance measured in the pressure apparatus at atmospheric pressure and 25° C and from the value of K obtained from the flat specimen.

The conductivity, γ, of a material is given by the equation

$$\gamma=BG \tag{2}$$

where G is the conductance of the specimen and B is the shape factor for conductivity. When the electric field is entirely within the

[2] BS Sci. Pap. 22, 398 (1927) S560; BS J. Research 11, 173 (1933) RP585.
[3] BS J. Research 14, 99 (1935) RP760.
[4] BS Sci. Pap. 22, 398 (1927) S560.

dielectric, the shape factor for conductivity is connected with the shape factor for dielectric constant by the equation

$$B=\frac{10^{21}A}{4\pi v^2}=\frac{A}{11.31} \tag{3}$$

where A is the shape factor for dielectric constant when the capacitance is measured in micromicrofarads, and v is the velocity of light in centimeters per second.[5]

The shape factors were corrected for changes in the dimensions of the specimens due to the compressibility of the materials. The compressibility of the copper or aluminum, of which the core was made, was so small that the effect of the change in the dimensions of the core was negligible. Correction was thus made only for the change in dimensions of the rubber, using the values of compressibility given in a former paper.[6]

III. PREPARATION OF SPECIMENS

Each of the carefully mixed rubber-sulphur compounds was formed in a seamless sheath about a wire. Some of the specimens were vulcanized in steam, while the rest were vulcanized in an inert gas. Those vulcanized in steam were dried before measuring.

1. MATERIALS INVESTIGATED

The rubber specimens investigated were vulcanized compounds of rubber and sulphur ranging in composition from 0 to 32 percent of sulphur. The percentages of sulphur were so chosen that the difference in sulphur content between successive specimens was in no case greater than 6 percent and in most cases it was 2 percent or less. Three varieties of rubber were used, "up-river fine Para", "smoked sheet", and purified rubber. The purified rubber was obtained by the process described by McPherson.[7]

The gutta-percha specimens were cut from a cable which had been obtained from a cable manufacturing company in England. This cable had been stored in water since its manufacture about 18 months before.

2. COMPOUNDING OF RUBBER

The rubber was usually mixed with the sulphur on a roll mill in air. In a few cases the mixing was done in an internal mixer in an atmosphere of carbon dioxide. The rubber and sulphur were weighed separately and the batch was weighed after mixing. The weight of the batch seldom differed from the sum of the weights of the constituents by more than 1 part in 1,000. Any greater difference was due to a loss of sulphur during the mixing and the requisite quantity of sulphur was added to correct for this loss.

[5] Since the ratio of the shape factors is the same regardless of the shape of the specimen, this ratio may be derived for the simplest case, i. e., a parallel plate capacitor. For this, neglecting edge effects, $K=C\times\frac{4\pi v^2 d}{10^{21}S}=AC$, and $\gamma=G\times\frac{d}{S}=BG$, where K is the dielectric constant, C is the capacitance in micromicrofarads, d is the thickness, S is the area of the electrode, v is the velocity of light, γ is the conductivity, and G is the conductance. Thus, $\frac{A}{B}=\frac{4\pi v^2}{10^{21}}=\frac{4\pi\times 9\times 10^{20}}{10^{21}}=11.31$.

[6] J. Research NBS 14, 99 (1935) RP760.

[7] BS J. Research 8, 751 (1932) RP449.

3. FORMATION OF SPECIMENS

Each specimen was formed by applying the rubber-sulphur compound concentrically about a wire by means of a commercial extrusion machine which had been adapted for this particular work. Since the various rubber-sulphur compounds could be applied smoothly to the wire in very narrow temperature ranges, it was necessary to control the temperature closely. For this purpose thermometers were placed at strategic points on the machine and an electric heater was added at the point where the insulated wire emerged, since it was not adequately heated by the original equipment. It was necessary to control the temperature by hand, but this could be readily done after a little experience.

4. VULCANIZATION OF SPECIMENS

Most of the specimens were packed in powdered talc and vulcanized in an atmosphere of steam while the others were vulcanized suspended in an atmosphere of dry hydrogen or CO_2 gas. The method of vulcanizing in steam was replaced by a method of vulcanizing in a dry gas when it was observed that some of the sulphur migrated from the rubber to the talc during vulcanization. Subsequent experiments showed that this migration was particularly significant when small samples of high sulphur content were vulcanized in contact with a considerable quantity of fresh talc.

Those specimens vulcanized in steam were coiled in a pan of powdered talc. This pan and its contents were then placed in a steam vulcanizer which had an automatic control on the steam pressure. The steam in the vulcanizer was maintained at the pressure corresponding to the desired vulcanizing temperature.

Those specimens which were vulcanized in an inert gas were placed in a 2-inch pipe, 6 meters in length, which was mounted vertically and which was provided with a steam jacket welded around it. The specimen was fastened at the top and suspended down the length of the pipe. A weight was fastened to the lower end of the specimen to keep it from touching the sides. The gas pressure around the specimen was kept slightly higher than the steam pressure at the vulcanizing temperature. If the pressure on the specimen were not kept above the pressure of the steam at the vulcanization temperature, the specimen became porous. This porosity was probably due to vaporization of the small amount of moisture present in the compound.

The specimens were vulcanized at 150° C for 4 to 15 hours. These relatively long times of vulcanization were used to assure the combination of practically all the sulphur.

5. DRYING OF SPECIMENS

The specimens which were vulcanized in steam were carefully dried before electrical measurements were made on them. Two methods of drying were used. Some of the specimens were placed in a sealed tank in which a vessel of concentrated sulphuric acid had been placed. This tank was kept at the temperature of 25° C while the air in it was kept stirred by a small fan. The specimens were kept in this tank

for 2 or 3 weeks. Other specimens were placed in a vacuum desiccator in which a drying agent had been placed. The desiccator was evacuated and the specimens left in this condition for 1 or 1½ weeks. All the specimens were stored in a dry atmosphere until measurements were made.

IV. APPLICATION OF PRESSURE TO SPECIMENS

The specimens, each of which was about 6 meters in length, were put in the pressure apparatus in such a way that one end was fastened to a special plug through which electrical contact was brought to the outside of the apparatus. An insulating compound was placed over the ends of the specimen to insulate the wire core from the pressure medium. The wire was used as one electrode in the electrical measurements while the pressure medium was used as the other.

1. APPARATUS FOR APPLYING PRESSURE TO SPECIMENS

A schematic drawing of the apparatus used for applying hydrostatic pressure to the specimens is shown in figure 1. It consisted of 3 parallel steel pipes 6 meters long of the grade known commercially as "double extra heavy." These pipes were connected together and to the pump and pressure gage by means of the proper fittings. The free end of each pipe was about 13 cm lower than the other end, which allowed the air to be removed from the system at the plug opening at the top of the apparatus.

This apparatus was designed so that either water or mercury could be used as the pressure medium around the specimen. The lowest pipe was provided for use with mercury. It was made the lowest part of the apparatus so that mercury could be placed in it around the specimen and yet the pressure could be transmitted from the pump to the surface of the mercury by water. The mercury was introduced through the opening in the top of the apparatus by means of a long-stemmed funnel. An electrical-contact system was used to determine when the proper level had been reached.

To facilitate the making of tight joints lead rings were used in the fittings wherever possible. The lead was forced firmly against the threads of the pipe by the set screws. Lead rings, however, could not be used in the part of the apparatus where mercury was used because of the action between mercury and lead. In this case the joints were made tight by heating the parts, applying "universal" wax and screwing them together while still hot. It was found possible to make the joints so tight that when a pressure of 700 bars [8] was applied to the system and the valve closed, the pressure would not decrease by more than 30 bars in 24 hours.

2. MOUNTING OF SPECIMENS

The specimens were mounted as shown in figure 1. The specimen extended down the length of the pipe and was connected at one end to the special plug. This plug, through which electrical contact was made to the core of the specimen, was so designed that the insulated terminal would not creep under the pressure used. A hard-rubber bushing, which was flared at the inner end, was screwed into a hole

[8] A bar is defined as 10^6 dynes per square centimeter and is equal to 0.987 normal atmosphere.

through the center of the steel plug. The bushing extended about 2½ cm beyond the outer end of the steel plug. The insulated terminal consisted of a brass rod which was flared on the inner end. This was screwed into a hole in the hard-rubber bushing. This terminal extended about 2½ cm beyond the bushing. A small threaded hole was placed in the flared end of the brass terminal and the wire core of the specimen was screwed into this.

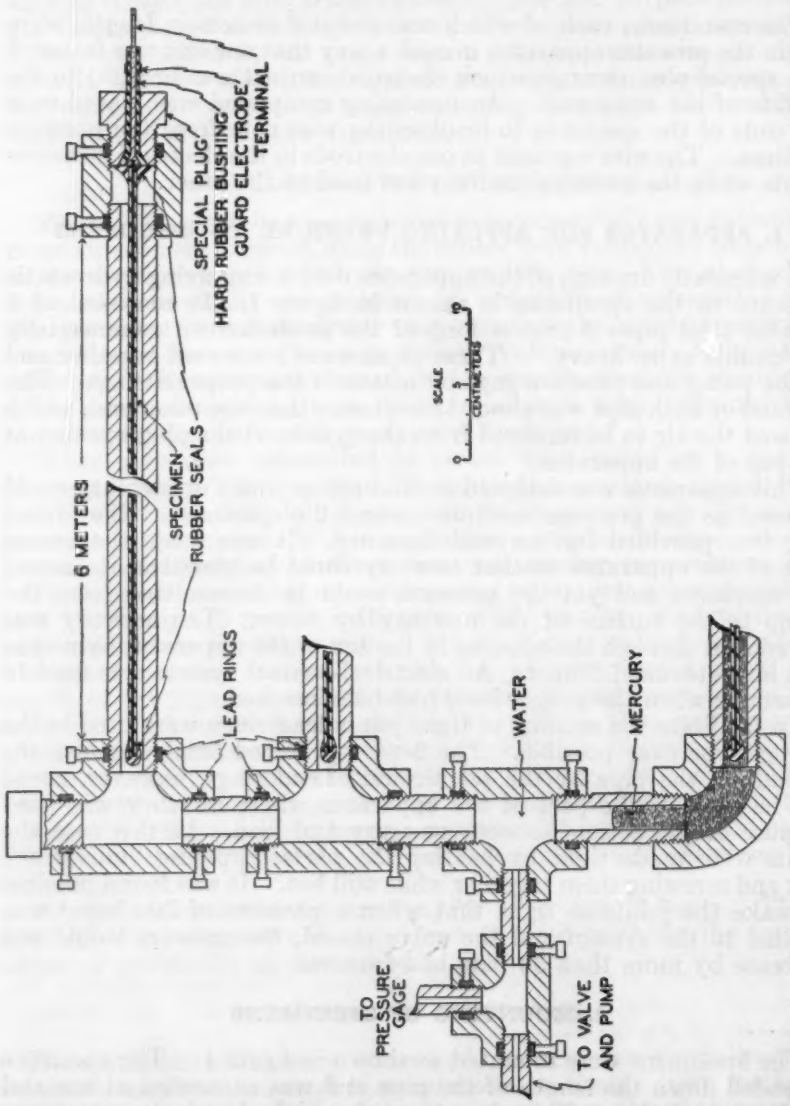

FIGURE 1.—*Apparatus for applying pressure to rubber specimens while electrical measurements are being made on them.*

The wire core, which was used as the inner electrode, was effectively insulated from the pressure medium at both ends by covering them with a thermoplastic insulating (DeKhotinsky) cement or a vulcanized-rubber mixture. The thermoplastic cement was used in the earlier measurements. Rubber was used later because it was found to be more reliable and durable.

The thermoplastic cement was applied by preheating the parts and working the softened material into place. When this material was used the coupling as well as the plug was removed from the pipe. The core of the specimen was attached to the inner end of the terminal in the plug. The coupling and plug were then heated to about 150° C and melted cement was poured over the face of the plug and around the specimen to a depth of about 2 cm. The cement was applied to the loose end of the specimen by heating it and working a ball of warm cement over it.

The rubber compound which was used to insulate the ends of the specimen core from the pressure medium was a soft, easily worked compound designed for rapid vulcanization. When this was used only the special plug was removed from the pipe. The end of this plug was coated with a thermoprene cement known commercially as Vulcalock Cement. After the core of the specimen had been attached to the terminal of the plug the soft unvulcanized-rubber compound was worked around the specimen and over the end of the plug, as shown in figure 1, with the aid of a little heat. A small ball of the rubber was also worked over the loose end of the specimen. The loose end and the plug were placed in an oven in such a way that only a few centimeters of the specimen were exposed to the heat of the oven. The oven was kept at a temperature of about 125° C until the compound was vulcanized.

V. ELECTRICAL MEASUREMENTS

The electrical measurements made on the specimens under pressure were the capacitance, power factor, and conductance.

1. CAPACITANCE AND POWER FACTOR

The capacitance and power factor were measured at 1,000 cycles per second by means of the modified Rosa bridge described by Scott, McPherson, and Curtis.[9] The capacitance between the wire core and the pressure medium surrounding the specimen was measured by a substitution method. Connections were made to the pipes and to the insulated terminal of the plug. This measurement included the capacitance in the plug, which was found to be of the order of 3 micromicrofarads. This excess capacitance was probably approximately counterbalanced by the decrease in capacitance of the specimen due to the sealing compound covering short lengths of the specimen at each end. About 1 cm was covered at the loose end, while about 1.5 cm was covered at the other end. While the exact error in capacitance due to the sealing compounds could not be determined, it was opposite in sign to the error due to neglecting the capacitance in the plug and it was assumed that the resulting error was negligible in comparison to the capacitance of the specimen which was usually about 2,000 micromicrofarads.

2. CONDUCTANCE

The conductance was measured by means of the direct deflection method described by Scott, McPherson, and Curtis.[10] A potential of 300 volts was used for this measurement. The readings were taken at the end of 1 minute after the potential was applied. Each

[9] BS J. Research 11, 173 (1933) RP585.
[10] See footnote 9.

specimen was short-circuited for 2 minutes before a measurement was made in order to eliminate the effect of the residual charge from previous electrifications. The guard electrode used in this measurement consisted of a piece of tinfoil wrapped tightly around the hard-rubber bushing as shown in figure 1. A fine wire was wrapped around the tinfoil to hold it in place and to afford a means of connecting it to the ground.

VI. RESULTS

The results were obtained under several different conditions. However, it was not thought advisable to divide the results into groups according to the different conditions which existed, since the variation between groups was no larger than that between the individual specimens of a single group. The composition of the various specimens and the conditions under which they were measured are given in table 1. The percentages of sulphur are given in the first column and the variety of rubber used is given in the second column. The third column gives the number of specimens of each which were measured. The kind of wire used as the core is given in the fourth column, and the method of vulcanization is given in the fifth column. The sixth column shows whether water or mercury was used as the pressure medium. The seventh column shows which of the specimens had the temperature controlled at 25° C during measurement, while the last column gives the gage which was used to measure the pressure.

The specimens were made from three varieties of rubber as was mentioned previously. No consistent difference between the specimens made from upriver fine Para and smoked sheet could be observed. As pointed out by Scott, McPherson, and Curtis the electrical properties of specimens made from purified rubber were slightly different from those made from unpurified rubber.[11] However, it was found that the change with pressure was about the same regardless of whether the rubber was purified or not. Because of this fact and because only four specimens made from purified rubber were measured, the results for these specimens were not grouped separately.

Two kinds of wire were used in preparing the specimens. Tinned copper wire was used in the earlier specimens, but when it was found that the tinning did not prevent action between the copper and the sulphur in the rubber, this was discarded in favor of aluminum wire. Comparison of results, however, failed to disclose any consistent difference between specimens made with the two kinds of wire.

Most of the pressure measurements were made with a pressure gage of the Bourdon tube type. This instrument was found to have errors as large as 10 percent which depended on whether the pressure had just been increased or decreased. The pressures were measured with the more accurate resistance pressure gage, described in a former paper, when this instrument became available.[12] However, measurements were made with this gage in only four cases. The measurements made with the Bourdon tube gage were corrected as best they could be but the inaccuracy of the pressure measurements is one of the sources of error in the results.

[11] BS J. Research 11, 173 (1933) RP585.
[12] J. Research NBS 14, 99 (1935) RP760.

TABLE 1.—*Composition of specimens and conditions of measurement*

Combined sulphur[a]	Rubber used	Number of specimens	Wire core	Vulcanized in—	Pressure medium	Temperature control	Pressure gage
Percent							
0	Fine Para	1	Copper		Mercury	None	Bourdon.
2	do	3	do	Steam	do	do	Do.
4	do	1	do	do	do	do	Do.
4.9	do	2	do	do	Water	do	Do.
[b]5	Smoked sheet	1	do	do	do	do	Do.
5.4	do	2	do	do	do	do	Do.
6	Fine Para	1	do	do	Mercury	do	Do.
6	Purified	1	Aluminum	CO_2	do	25° C	Resistance.
8	do	1	do	do	do	do	Do.
8	Fine Para	1	do	Hydrogen	do	None	Bourdon.
8	do	1	Copper	Steam	do	do	Do.
[b]8.5	Smoked sheet	1	do	do	Water	do	Do.
[b]10	do	2	do	do	do	do	Do.
10	Fine Para	1	do	do	Mercury	do	Do.
10	do	1	Aluminum	do	do	do	Do.
10	Purified	1	do	CO_2	do	25° C	Resistance.
[b]11.5	Smoked sheet	1	Copper	Steam	Water	None	Bourdon.
12	Purified	1	Aluminum	CO_2	Mercury	25° C	Resistance.
12	Fine Para	1	do	Hydrogen	do	None	Bourdon.
[b]13	Smoked sheet	1	Copper	Steam	Water	do	Do.
13.5	Fine Para	1	do	do	Mercury	do	Do.
13.5	do	1	Aluminum	do	do	do	Do.
[b]14.5	Smoked sheet	1	Copper	do	Water	do	Do.
16	Fine Para	1	do	do	Mercury	do	Do.
[b]16	Smoked sheet	1	do	do	Water	do	Do.
[b]17.5	do	1	do	do	do	do	Do.
18	Fine Para	2	do	do	Mercury	do	Do.
18.1	do	2	do	do	Water	do	Do.
19	do	1	do	do	Mercury	do	Do.
19	do	1	Aluminum	do	do	do	Do.
[b]19	Smoked sheet	1	Copper	do	Water	do	Do.
20	Fine Para	1	do	do	Mercury	do	Do.
22	do	1	do	do	do	do	Do.
[b]24	Smoked Sheet	1	do	do	Water	do	Do.
26	Fine Para	1	do	do	Mercury	do	Do.
32	do	1	do	do	do	do	Do.
32	Smoked sheet	2	do	do	Water	do	Do.

[a] The sulphur content was assumed to be that which was mixed into the compound in all cases, except for 4.9, 5.4, and 18.1 percent of sulphur. These specimens were analyzed for sulphur when it was discovered that sulphur migrated to the talc during vulcanization in steam. The other specimens vulcanized in steam were not then available for analysis.

[b] These specimens were not measured through a pressure cycle until after they had been under pressure for about a month.

Another source of error in the results is the lack of temperature control. Most of the measurements had been made before the importance of temperature control was realized. Only the last four specimens were measured under controlled-temperature conditions. The temperatures of the other specimens varied from 18.5 to 26.5° C. with most of the measurements being made at temperatures between 20 and 22° C.

The two pressure media, water and mercury, were used so that the possible effect of water absorption might be studied. Measurements with mercury as the pressure medium gave results for the specimen in the dry condition. With water as the pressure medium the effect of progressive water absorption could be studied.

2. DIELECTRIC CONSTANT

The effect of pressure on the dielectric constant is shown in figure 2, where the dielectric constants at atmospheric pressure (approximately 1 bar) and 700 bars are plotted as functions of the sulphur content.

These curves were obtained from measurements made on the 34 specimens immediately after they had been placed in the apparatus. The curve for 1 bar is the same as that reported in the paper by Curtis, McPherson, and Scott.[13] The irregularity of the measured values at 1 and 700 bars is about the same. At 700 bars two-thirds of the specimens yielded values which agreed with the values given by the curve within 1 percent. The difference was greater than 2 percent in only six cases. The maximum difference was 6 percent which was obtained for the specimen containing 18.1 percent of sulphur.

Increasing the pressure moved the maximum to lower percentages of sulphur and decreased the height of the maximum. This is the same effect as was obtained by decreasing the temperature as reported by Scott, McPherson, and Curtis.[14] A change of 700 bars pressure

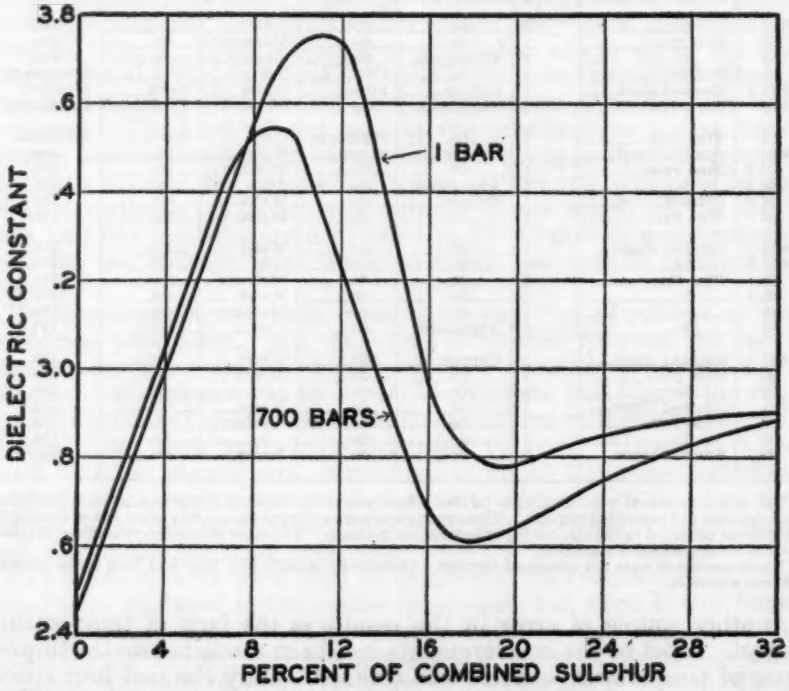

FIGURE 2.—*Change of the dielectric constant of rubber-sulphur compounds with sulphur content, at 1 and at 700 bars.*

had the same effect as a change in temperature of 12 to 20° C., the average being about 16° C. The dielectric constant for specimens containing up to about 7.5 percent of sulphur was increased slightly by pressure. For higher percentages of sulphur the dielectric constant was decreased by pressure. The maximum change with pressure occurred for about 12 percent of sulphur, while for 32 percent of sulphur the decrease with pressure was small.

The dielectric constant was, in most cases, a linear function of the pressure between 1 and 700 bars pressure. There were two ranges of

[13] BS Sci. Pap. 22, 398 (1927) S560.
[14] BS J. Research 11, 173 (1933) RP585.

sulphur content where it was not a linear function of the pressure, one range being between about 8 and 10 percent of sulphur and the other being between about 16 and 24 percent of sulphur. The results for a few representative specimens are shown in figure 3 where the dielectric constants are plotted against the pressure. Two of these, 0 and 4 percent of sulphur, were selected from the sulphur range where the dielectric constant was increased by pressure. The total increase for a pressure change of 700 bars was small, but the increase of the dielectric constant with pressure was uniform. The specimen containing 8 percent of sulphur came at about the boundary between the sulphur range where the dielectric constant increased with pressure and the

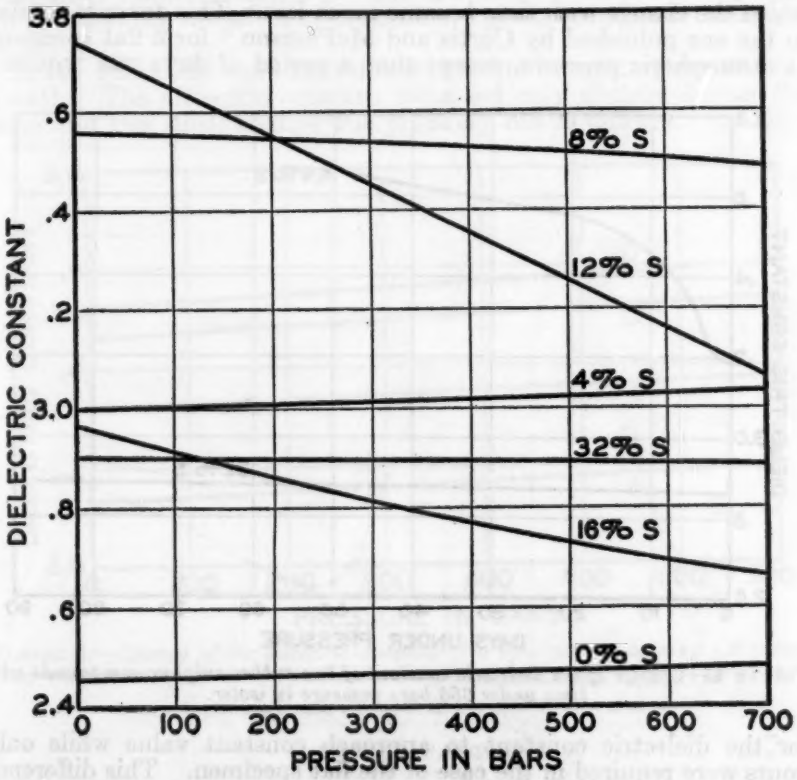

FIGURE 3.—*Change of the dielectric constant of various rubber-sulphur compounds with pressure.*

sulphur range where the dielectric constant decreased with pressure. This was also in one of the ranges where the dielectric constant was not a linear function of the pressure. The change with pressure was small for this specimen but was larger at the high pressures than at the low pressures. Three specimens, 12, 16, and 32 percent of sulphur, were selected from the sulphur range where the dielectric constant decreased with pressure. For 12 and 32 percent of sulphur, the dielectric constant was a linear function of the pressure, but for 16 percent of sulphur, the change with pressure became less as the pressure was increased.

The specimens for which water was used as the pressure medium were kept under pressure for a month or more to determine the effect which this would have on the change of the electrical properties with pressure. It was found that for the specimens containing low percentages of sulphur the electrical properties changed with time under pressure, but that for specimens containing over 18 or 20 percent of sulphur there was little change. The results for two representative specimens are shown in figures 4 and 5. Figure 4 shows the change of the dielectric constant of specimens containing 4.9 and 32 percent of sulphur with time under 655 bars pressure. The dielectric constant of the specimen containing 4.9 percent of sulphur increased rapidly with the time under pressure for the first few days, after which the change with time became much less. This curve is similar to the one published by Curtis and McPherson [15] for a flat specimen at atmospheric pressure, except that a period of days was required

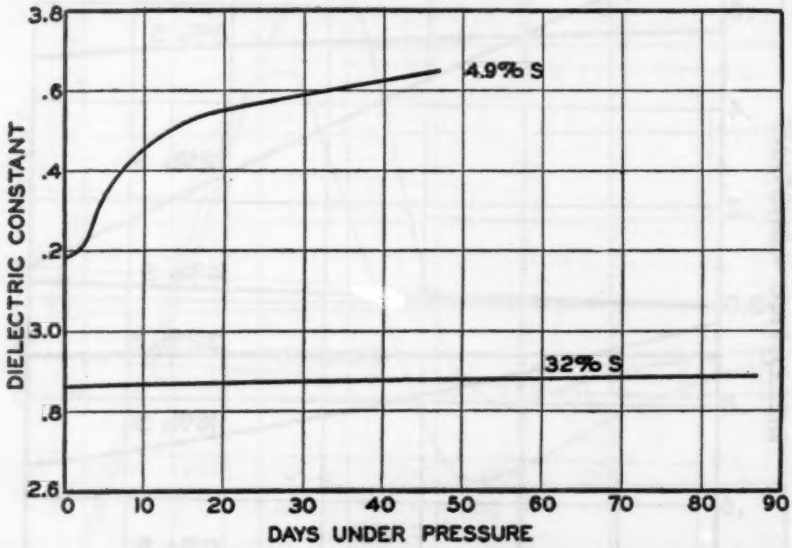

FIGURE 4.—*Change of the dielectric constant of two rubber-sulphur compounds with time under 655 bars pressure in water.*

for the dielectric constant to approach constant value while only hours were required in the case of the flat specimen. This difference in time may, in part, be accounted for by the fact that the flat specimen was thinner than the cylindrical specimen and that it was exposed to water on both sides while the cylindrical specimen had only one surface exposed to the water. The difference in composition of the specimens may have been an added factor in this difference in time. The curve in figure 4 is of the same type as that obtained by Lowry and Kohman [16] for absorption of water under pressure. The change of the dielectric constant with time under pressure, therefore, seems to be a function of the water absorption alone.

The dielectric constant of the specimen containing 32 percent of sulphur did not change materially with time under pressure. This

[15] Tech. Pap. BS 19, 718 (1925) T299.
[16] J. Phys. Chem. 31, 23 (1927).

was to be expected if the dielectric constant is a function of the water absorption, since hard rubber absorbs very little moisture.

Figure 5 shows the manner in which the dielectric constant of the specimen containing 4.9 percent of sulphur changed with pressure after various lengths of time under pressure in water. The curves are practically parallel, which shows that the effect of pressure is about the same regardless of the time that the specimen has been under pressure. If the only effect of continued pressure under water is the absorption of water by the rubber, then this is equivalent to saying that the effect of pressure is about the same regardless of the amount of water absorbed. The dielectric constant of the specimen containing 32 percent of sulphur changed so little with time under pressure that no curves showing the effect of pressure are given other than the one in figure 3.

A few specimens were kept under pressure in mercury for about a month. The dielectric constant increased only slightly during this time and this small change was probably not significant.

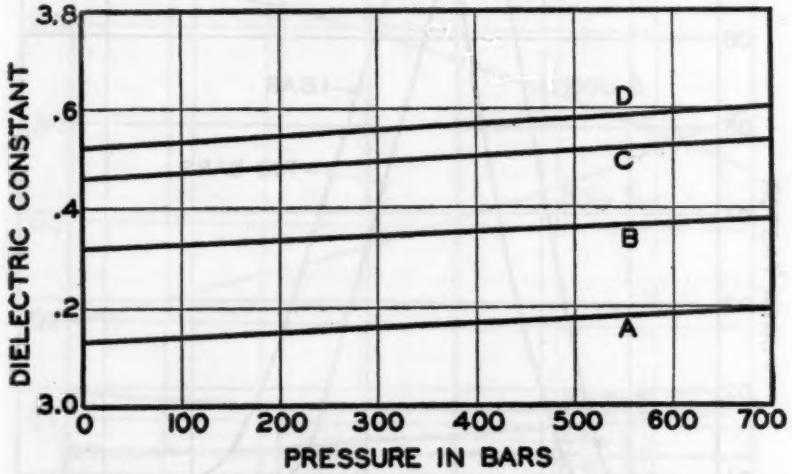

FIGURE 5.—*Change of the dielectric constant of a specimen containing 4.9 percent of sulphur with pressure after different lengths of time under 655 bars pressure.*

A, at beginning; B, after 6 days; C, after 18 days; D, after 33 days.

2. POWER FACTOR

The effect of pressure on the power factor is shown in figure 6 where the power factors at 1 and 700 bars are shown as functions of the sulphur content. These curves were drawn as average curves through the plotted points. The irregularity of the power factor values was large compared with the irregularity of the dielectric constant values. Of the 34 specimens which were measured, 10 had values of the power factor which differed from the values on the curve by more than 20 percent. Of these, 5 differed by more than 40 percent. Two of these latter specimens, 1 of which contained 6 percent of sulphur and the other 18.1 percent of sulphur, had power factors which differed from the values on the curve by about 85 percent. This irregularity was larger than was obtained for the flat specimens at atmospheric pressure.

Increasing the pressure moved the maximum to lower percentages of sulphur. The height of the maximum apparently was not changed by pressure. This was the same type of change that was observed by Scott, McPherson, and Curtis for a change in temperature.[17] The amount of the change brought about by an increase of 700 bars was about the same as was obtained for the temperature changes determined for the dielectric constant.

Although the irregularity of the measured values was large, the character of the change with pressure was consistently that represented by these curves. The power factors of all the specimens containing up to 2 percent of sulphur were very nearly independent of

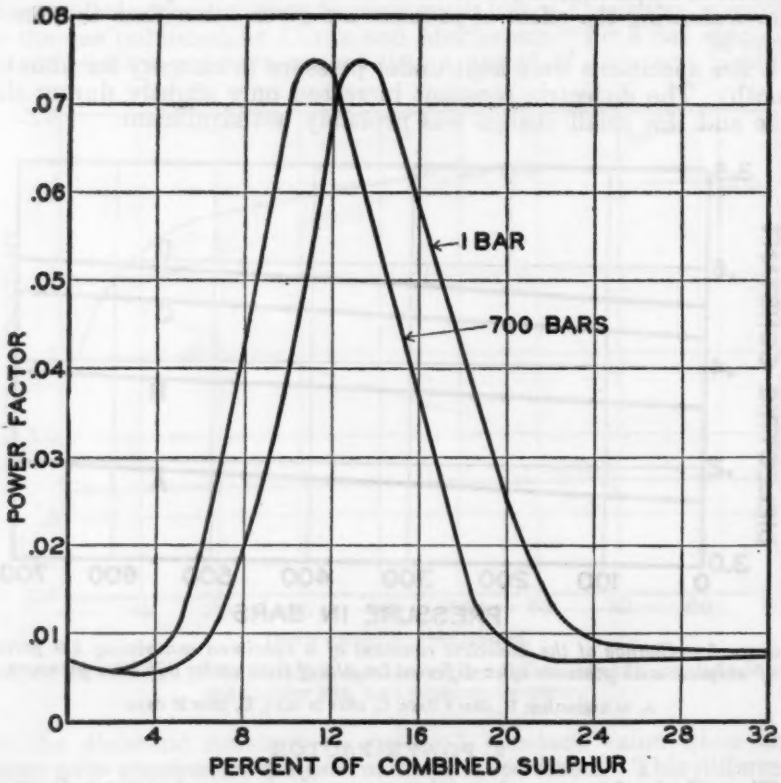

FIGURE 6.—*Change of the power factors of rubber-sulphur compounds, at 1 and at 700 bars, with sulphur content.*

pressure. The power factors at 700 bars were higher than those at 1 bar for all the specimens containing from 4 to about 12 percent of sulphur, while for percentages of sulphur higher than this, the power factors at 700 bars were lower than at 1 bar, with one exception. The values of the power factors of specimens containing 13.5 percent of sulphur increased with pressure at the low pressures and decreased with pressure at high pressures, so that the values at 700 bars were about those at 1 bar. This does not agree with figure 6.

[17] BS J. Research 11, 173 (1933) RP585.

The power factor was a nonlinear function of the pressure in most cases for pressures between 1 and 700 bars. The manner in which the value of the power factor varied with the pressure is shown in figure 7 where the power factors for a few representative specimens are plotted against the pressure. The specimen containing no sulphur was selected from the sulphur range where the power factor was unaffected by pressure. The specimens containing 4 and 8 percent

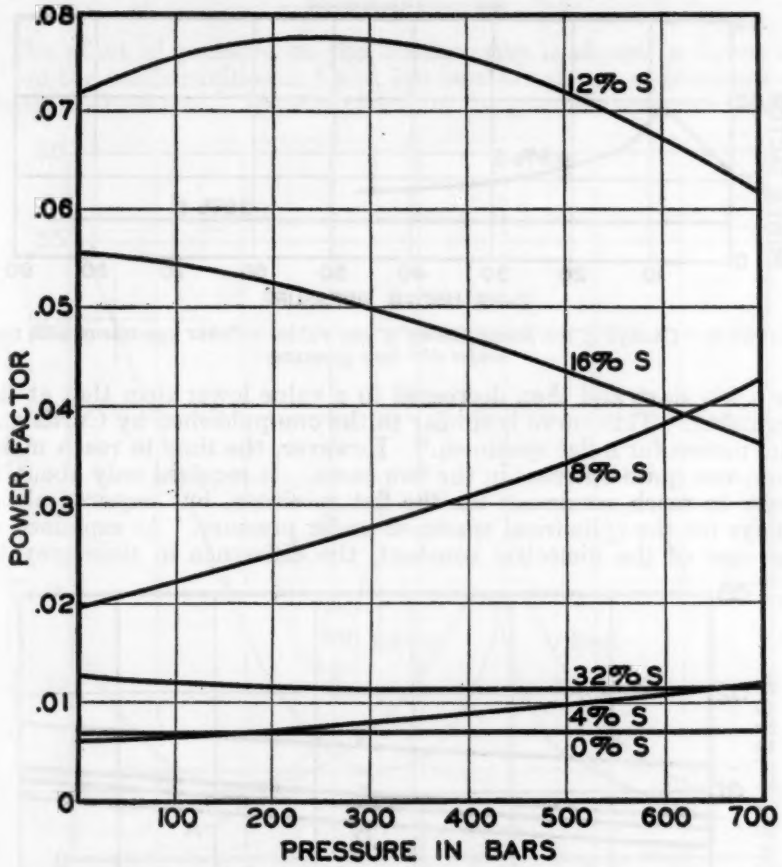

FIGURE 7.—*Change of the power factors of various rubber-sulphur specimens with pressure.*

of sulphur were selected from the range where the power factor increased with pressure. The curves for these are concave upward. The specimen containing 12 percent of sulphur was in the range where the power factor passed through a maximum with pressure. The curve for this specimen is concave downward and the maximum occurs at about 250 bars. The specimens containing 16 and 32 percent of sulphur are from the sulphur range where the power factor decreased with pressure. The curve for 16 percent of sulphur is concave downward while that for 32 percent of sulphur is concave upward. In only one other case beside those for 0 and 2 percent of sulphur was there indication that the power factor was a linear function of the pressure. The power factors of 2 of the specimens con-

taining 10 percent of sulphur were linear functions of the pressure. The power factor of the third, which was made from purified rubber, was not a linear function of the pressure and its curve was concave downward.

The change of the power factor with time under a pressure of 655 bars in water is shown for two specimens in figure 8. The power factor of the specimen containing 4.9 percent of sulphur increased

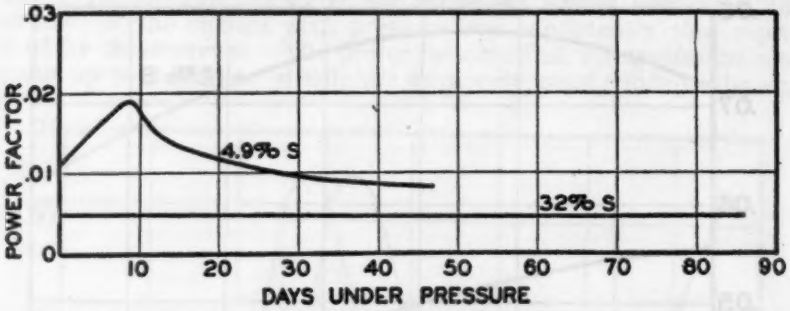

FIGURE 8.—*Change of the power factors of two rubber-sulphur specimens with time under 655 bars pressure.*

for a few days and then decreased to a value lower than that at the beginning. This curve is similar to the one published by Curtis and McPherson for a flat specimen.[18] However, the time to reach maximum was quite different in the two cases. It required only about 10 hours to reach maximum for the flat specimen, but required about 9 days for the cylindrical specimen under pressure. As explained in the case of the dielectric constant, the difference in time may be

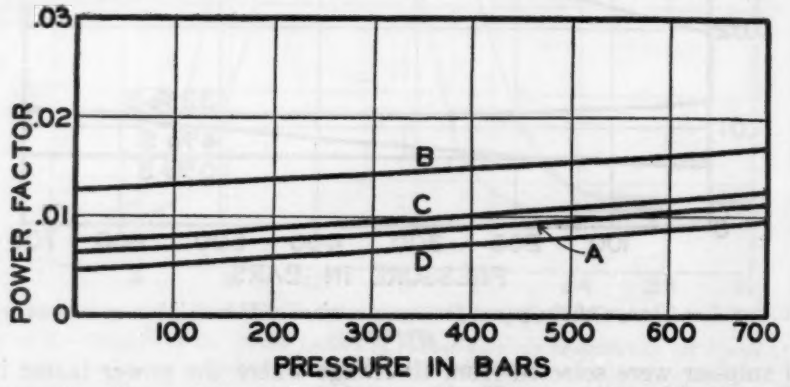

FIGURE 9.—*Change of the power factor of a rubber-sulphur specimen containing 4.9 percent of sulphur with pressure after different lengths of time under 655 bars pressure.*

A, at beginning; B, after 6 days; C, after 18 days; D, after 33 days.

due to the difference in shape and composition. The power factor of the specimen containing 32 percent of sulphur did not change appreciably with time under pressure.

The manner in which the power factor of the specimen containing 4.9 percent of sulphur changed with pressure after various periods under pressure is shown in figure 9. These curves are slightly con-

[18] Tech. Pap. BS 19, 718 (1925) T299.

cave upward but are approximately equidistant from each other at all pressures. Thus, the only effect of time under pressure was to change the values but not to change the slopes of the curves. The curves for the specimen containing 32 percent of sulphur were practically unaffected by time under pressure and so no curves are shown for it, except the one in figure 7.

3. CONDUCTIVITY

The effect of pressure on the conductivity is shown in figure 10 where the conductivities at 1 and 700 bars are shown as functions of the sulphur content. These curves show the general average of values,

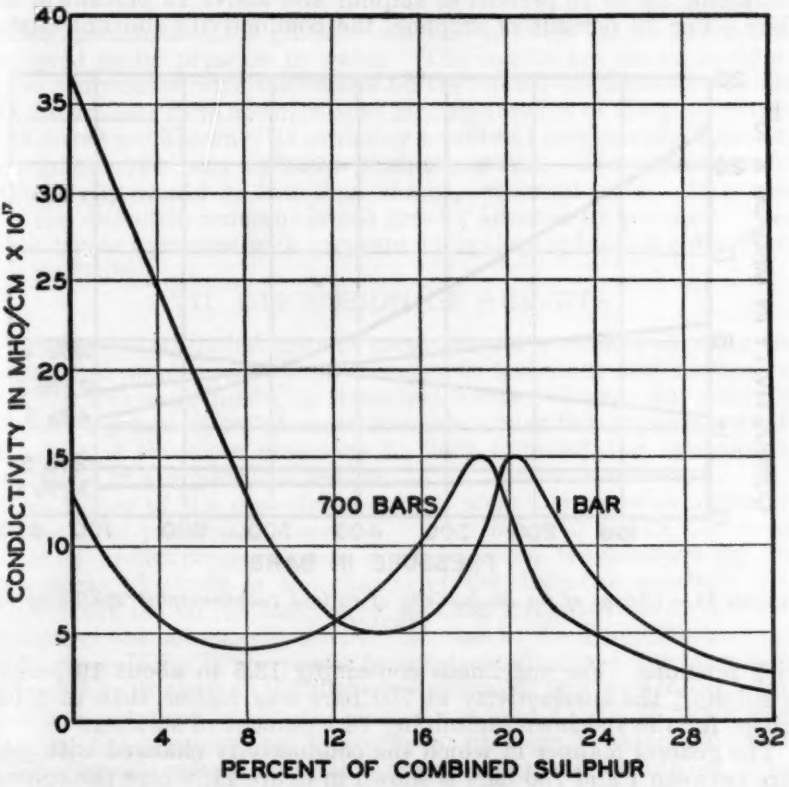

FIGURE 10.—*Change of conductivities of rubber-sulphur compounds at 1 and 700 bars with sulphur content.*

although the irregularity of the measured values was large. About half of the specimens had measured conductivities which differed at 1 or 700 bars from the curve values by more than 40 percent. Of these, 5 specimens had conductivities which differed from the curve values by more than 60 percent. In one case the difference was more than 80 percent. The conductivity of the single specimen containing no sulphur at 1 bar exceeded the value shown on the curve by about 230 percent. The value shown on the curve is in agreement with the measurements on flat specimens.

The maximum of the conductivity curve was moved to lower percentages of sulphur by increased pressure as were the maxima for dielectric constant and power factor. This change is in the same direction as was obtained by Scott, McPherson, and Curtis, for a decrease in temperature.[19] The change with pressure at low percentages of sulphur has no counterpart in the change with temperature as observed by them, since the conductivities of the specimens made from purified rubber, which they used, were about as low in the low-sulphur range as in the high-sulphur range.

Although the irregularity in results was large, the sign of the change with pressure was nearly always that indicated by the curves. The conductivity at 700 bars was lower than at 1 bar for all specimens containing up to 10 percent of sulphur and above 19 percent of sulphur. For 12 percent of sulphur, the conductivity did not change

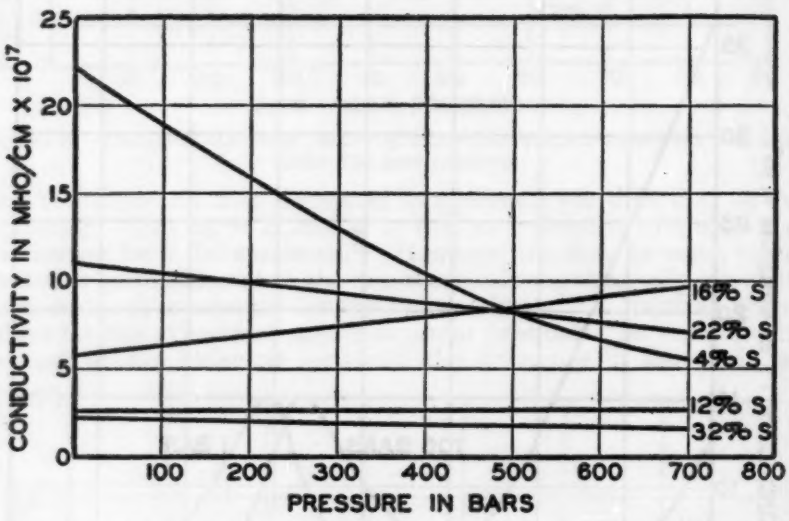

FIGURE 11.—*Change of the conductivity of various rubber-sulphur specimens with pressure.*

with pressure. For specimens containing 13.5 to about 19 percent of sulphur, the conductivity at 700 bars was higher than at 1 bar, except for the specimen containing 18.1 percent of sulphur.

The general manner in which the conductivity changed with pressure between 1 and 700 bars is shown in figure 11, where the conductivities of a number of representative specimens are plotted against the pressure. The specimen containing 4 percent of sulphur was selected from the low-sulphur range, where the conductivity decreased with pressure. The curve for this specimen is concave upward, as are the curves for all the specimens except one in this range. The curve for one of the specimens containing 2 percent of sulphur was apparently a straight line. The specimen containing 12 percent of sulphur came between the two ranges, in one of which the conductivity decreased with pressure and in the other increased with pressure.

[19] BS J. Research 11, 173 (1933) RP585.

The conductivity of this specimen was independent of pressure. The specimen containing 16 percent of sulphur was selected from the sulphur range where the conductivity increased with pressure, and the specimens containing 22 and 32 percent of sulphur were selected from the high-sulphur range where the conductivity decreased with pressure. Except in the first range, the conductivity was generally a linear function of the pressure. The few exceptions are probably not significant since duplicate specimens would have conductivities, one of which was a linear and the other a nonlinear function of the pressure.

4. DIELECTRIC CONSTANT, POWER FACTOR, AND CONDUCTIVITY OF GUTTAPERCHA

Two specimens of the guttapercha used in cable manufacture were measured under pressure in water. The results are shown in figure 12 for comparison with the results on the rubber-sulphur compounds. The dimensions were not corrected for compression of the guttapercha since it was not known. It probably would not decrease the dielectric constant at 700 bars by more than 2 percent. The correction for conductivity would be less than the experimental error. It is seen that the dielectric constant is not greatly affected by pressure. The power factor increased with pressure while the conductivity decreased with pressure.

VII. DISCUSSION OF RESULTS

This investigation has been in progress over a number of years and during that time several improvements in technique and methods of measurement were made, as described above. It was not practical to make a complete set of measurements under the improved conditions. It is therefore necessary to keep in mind the variation in conditions in studying the results.

The values of the dielectric constant were the most consistent of the electrical properties measured. As mentioned above, the measurements under pressure were made at room temperature for the most part. A study of the change of the dielectric constant with temperature led to the conclusion that the irregularities of the temperature could not explain the irregularities in the dielectric constant.

The irregularity in the power factor determinations was very large compared with that of the dielectric constant and was much larger than was obtained by Scott, McPherson, and Curtis in their work with the flat specimens at atmospheric pressure.[20] A consideration of the temperatures at which the measurements were made led to the conclusion that only a part of the irregularity in power-factor determinations could be accounted for by the diversity of temperatures.

It is possible that a part of the irregularity observed in the values of the electrical properties is due to an inaccurate assignment of composition. The amount of sulphur in the specimen was assumed to be that which was put into the mixture. Late in the investigation it was found that in some cases significant amounts of sulphur migrated from the rubber compound into the talc during vulcanization in steam. Thus, the composition of the cylindrical specimen was not the same as the flat specimen made from the same batch of mixture. Most of

[20] BS Sci. Pap. 22, 398 (1927) S560.

the specimens had deteriorated so badly that they had been discarded before it was realized that an analysis should have been made. The six specimens that were vulcanized suspended in an inert gas suffered no significant loss of sulphur during vulcanization. The assigned sulphur contents of the others may be in error by varying amounts. Even this, however, would not explain all the irregularity in the results of the power factor determinations. In two cases, supposedly

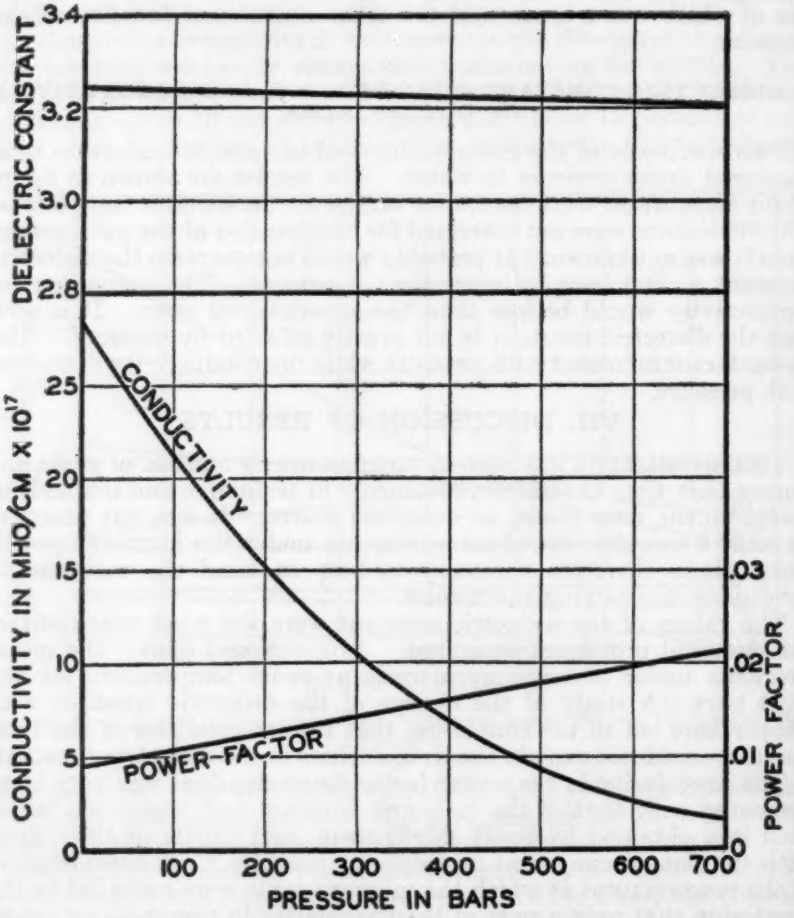

FIGURE 12.—*Change of the dielectric constant, power factor, and conductivity of guttapercha with pressure.*

identical specimens having about the same value of the power factor at 1 bar had quite different values at 700 bars.

The irregularity in the results of the conductivity determinations was no greater than might be expected from such measurements. It is significant, however, that the value of the conductivity decreased with pressure in rather definite sulphur ranges and increased with pressure in other ranges.

Only a negligible part of the power factor can be accounted for by the 1-minute conductivity. Assuming the specimen having the highest conductivity to be a perfect capacitor in parallel with a conductance equal to the 1-minute conductivity of the specimen, the computed power factor due to this conductance would be about 1×10^{-6}. This is about $\frac{1}{1000}$ of the lowest power factor which was measured.

The outstanding feature of these results is that the effect of pressure is not the same for all ranges of sulphur content. Each of the three electrical properties measured increased with pressure in certain sulphur ranges and decreased with pressure in other ranges. The changes were such that the maximum for each property was moved to lower percentages of sulphur with increased pressure. It is quite evident from this that some phenomenon other than a change in density is occurring.

These results can be qualitatively explained by the dipole or an equivalent theory as first suggested by Kitchen to explain the changes with temperature.[21] Under the dipole theory, the curves for dielectric constant in figure 2 are explained as follows: The rubber molecule is nonpolar. The addition of sulphur to the rubber molecules produces dipoles which presumably reside in the carbon-sulphur linkages and which thus increase the dielectric constant by amounts which are proportional to the combined sulphur. This explains the linear relationship between the dielectric constant and percentage of sulphur between 0 and about 9 percent of combined sulphur at the pressure of 1 bar. However, the hardness of the rubber also increases with the sulphur content. This increases the restrictive forces on the dipoles and at certain percentages of sulphur these forces seriously interfere with the motions of the dipoles so that they cannot readily follow the electric field at the frequency used in the measurement of the dielectric constant. Thus, the dielectric constant is not as large as it would be if the dipoles were able to move freely. As still more sulphur is added the rubber becomes harder, the motions of the dipoles are more restricted and the dielectric constant is thus decreased, although the number of dipoles has been increased. When sufficient sulphur has been added so that the restrictive forces on the dipoles allow only a negligible motion of the dipoles, the dielectric constant is due only to the separation of the charges in the atom and the relatively flat portion of the curve above about 19 percent of sulphur at 1 bar is obtained.

Scott, McPherson, and Curtis have shown that this curve is modified by changes in temperature.[22] The maximum is decreased and moved to a lower percentage of sulphur by a decrease in temperature. The same effect was produced by an increase of pressure as is shown in figure 2. Decreasing the temperature and increasing the pressure both make the rubber harder, which means that the restrictive forces on the dipoles have been increased. In the low-sulphur range the restrictive forces are still negligibly small for the frequency used. The dielectric constant in this range is slightly increased by a decrease of temperature or an increase of pressure because of the closer packing of the molecules. In the sulphur range where the restrictive forces are large enough to appreciably interfere with motions of the dipoles, that is, above about 8 percent of sulphur, an increase of the restrictive

[21] J. Am. Inst. Elec. Eng. 48, 281 (1929).
[22] BS J. Research 11, 173 (1933) RP585.

forces, brought about by a decrease in temperature or an increase in pressure, materially decreases the motion of the dipoles, thereby decreasing the dielectric constant.

On the basis of the dipole theory, the part of the power factor represented by the peaks in the curves in figure 6 is due to the dipoles. The energy loss in the dielectric, which is due to the dipoles, is proportional to the product of the amount of motion of the dipole and the resistance to motion which it encounters. Thus, at low percentages of sulphur, the dipole contributes a negligible amount to the power factor since the restrictive forces on the dipole are negligible and the dipole rotates freely with the electric field. The low power factor which is obtained is due to other causes. At high percentages of sulphur the dipole contributes a negligible amount to the power factor since the restrictive forces are so great that only negligible motion of the dipole is possible. Here, again, the low power factor which is obtained is due to other causes. In the intermediate-sulphur range where motion of the dipole and an appreciable resistance to its motion are both present, the power loss due to the dipole is added to the loss due to other causes and a peak is obtained in the power-factor curve.

The peak of the power-factor curve is modified by temperature in a manner similar to pressure. Scott, McPherson, and Curtis have shown that the maximum is moved to a lower percentage of sulphur by a decrease in temperature. It will be seen, from figure 6, that an increase in pressure gives the same effect. On the low-sulphur side of the peak, where the restrictive forces are so small that the dipoles are still able to approximately follow the electric field, an increase in the restrictive forces increases the power factor. On the other side of the peak, where the restrictive forces are so large that the dipoles can only partially follow the electric field, an increase in the restrictive forces materially decreases the motions of the dipoles, thereby decreasing the power factor.

The similarity of the behavior of the maximum for the conductivity to that of the power factor suggests the idea that the part of the conductivity represented by the maximum might be due to dipole motion. This would mean that for certain values of the restrictive forces the dipoles rotate so slowly under the force of the applied field that they are still yielding at the end of 1 minute. The change of the restrictive forces on the dipoles by temperature or pressure changes would move the maximum in a manner similar to that shown in figure 10. The high values of the conductivity at the low percentages of sulphur are probably due to impurities which can be eliminated by purification of the rubber, since the curve for the conductivity of specimens made from purified rubber and sulphur given by Scott, McPherson, and Curtis does not rise appreciably at the low-sulphur end.

WASHINGTON, March 13, 1935.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP807

Part of Journal of Research of the National Bureau of Standards, Volume 15, July 1935

IRON GALLATE INKS—LIQUID AND POWDER

By Elmer W. Zimmerman

ABSTRACT

A study was made of iron gallate ink that contained 3 grams of iron per liter. Both ferric and ferrous salts and various solid acids were used. Three ink formulas were devised, one for ferric and two for ferrous salts. These inks do not deposit sediment readily and they are a little less corrosive to steel pens than the Government standard writing ink. Two of the formulas can be used to prepare ink powders that will comply with the requirements of Federal Specification TT–I–563, Ink; Writing.

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I. INTRODUCTION

Writing ink purchased by the U. S. Government under the specification [1] for this material is most commonly obtained in liquid form ready for use. The specification also includes ink in the form of a concentrated liquid or a powder. Concentrated inks have been used to some extent because their compactness facilitates distribution from a central purchasing agency. Ink powders are preferred for the same reason, but prior to 1932 all the powders submitted for tests failed to comply fully with the requirements of the specification. Some powders produced ink that was not of the iron gallotannate type, while the ink made from those which were of the iron gallotannate type lacked sufficient stability.

Writing inks purchased under the specification have not always given satisfactory service. The U. S. Post Office Department has complained at various times about the excessive corrosion of steel pens caused by the ink used in their stations. As a result, a general study of writing inks was undertaken in an attempt to prepare one that would be less corrosive to steel pens than the standard ink,

[1] Federal Specification TT–I–563, Ink; Writing (see table 1 for formula).

and which could be prepared in the form of a powder and still comply with the requirements of the specification.

An iron gallotannate ink is considered permanent because it contains iron. If and when the black iron tannate or gallate decomposes, the iron remains and can be used to restore the writing. The standard writing ink contains 3 g of iron per liter, and in order to have all the experimental inks on the same basis, this figure was used throughout the work. With this concentration of iron as a starting point, the other ingredients necessary to make an ink were studied by varying their concentrations or by substituting different types of materials. The characteristics of the experimental inks were determined by using the tests described in the specification. An attempt was made to evaluate the stability in terms of the number of days required for sediment to appear. The results obtained for any one ink were not strictly reproducible, but in testing a series of inks simultaneously, the results always placed the inks in the same order of stability. Finally three inks were prepared which were less corrosive to steel pens and more stable than the standard writing ink.

II. EFFECT OF ALTERING COMPOSITION WITH RESPECT TO CERTAIN INGREDIENTS

1. PHENOLIC BODY

The formula for the U. S. Government standard writing ink was derived from the formula for the standard record ink by halving the quantities of all the materials except the dye and phenol. The formula for standard record ink is almost identical with the one recommended by O. Schluttig and G. S. Neumann,[2] who made a very careful study of the subject.

Schluttig and Neumann showed that ink made with gallic acid produces writing that darkens more than that produced by ink made with other phenolic materials that give colored compounds with ferric salts. Since the amount of gallic acid they needed to prepare a liter of ink was larger than the amount of this substance that would dissolve in a liter of water, tannic acid was added to make up the difference. In their final ink, Schluttig and Neumann used 23.4 g of tannic acid and 7.7 g of gallic acid, with 30 g of ferrous sulphate, in 1 liter of ink. This ink contained 1.05 gram-moles of phenolic compounds for every gram-atom of iron.

Silbermann and Ozorovitz[3] made a study of iron gallates and prepared a compound requiring 1 gram-mole of gallic acid for every gram-atom of iron. Their object apparently was to study the iron gallate compounds in the ink before it was put on paper.

Some time later F. Zetsche[4] and his collaborators made a study of written characters. Their approach involved an oxidation reaction taking place in a dilute solution. The ink compound which they prepared from gallic acid was formed from 1 gram-mole of gallic acid and 1 gram-atom of iron. In order to check this point for the present work, two preparations were made. In the first, equimolecular quantities of ferric chloride and gallic acid were dissolved separately in alcohol and these solutions were mixed. In the second, 2 moles of

[3] Die Eisengallustinten, v. Zahn & Jaensch, Dresden (1890).
[2] Bucarest. Bul. soc. stiinte 17, 43–57 (1908); Chem. Zentr. 1908 II, 1024.
[4] Ann. Chem. 435, 233 (1924).

ferric chloride and 1 mole of gallic acid were used. Both precipitates contained approximately the same proportion of iron, which corresponded to the theoretical amount of iron in ferrigallic acid.

Inks have been made which contain a higher concentration of gallic acid than could be possible if the solubility of this material in water were the controlling factor. The U. S. Government formerly bought "Treasury Standard" copying ink that was based on a formula requiring 15.4 g of gallic acid per liter.[5] An experimental ink showed that as much as 18 g of gallic acid can be dissolved in a liter of water containing 15 g of ferrous sulphate. Only 10 g of gallic acid is necessary if the ink is to contain 3 g of iron per liter.

It is well known that gallic acid inks have better keeping qualities than inks made with tannic acid, and since a sufficient quantity of gallic acid can be dissolved in a solution containing ferrous sulphate equivalent to 3 g of iron per liter, to make an ink, it is logical to eliminate the tannic acid. Inks prepared with decreasing amounts of tannic acid accompanied by increasing amounts of gallic acid were tested for stability, and the results are given in table 1. Those inks which contained gallic acid without tannic acid had the best keeping qualities.

TABLE 1.—*Effect of gallic and tannic acid on stability of ink*

Ink no.	Composition of ink in grams per liter of water						Stability in approximate days for sediment to form
	Tannic acid	Gallic acid	Ferrous sulphate, $FeSO_4.7H_2O$	Ferric sulphate, anhydrous	Oxalic acid	Tartaric acid	
1[a]	11.7	3.8	15			2.6	5
2	8.4	7.7	15			2.6	5
3		10	15			2.6	10
4	11.7	3.8		10.7	2.16		7
5	8.4	7.7		10.7	2.16		35
6		10		10.7	2.16		[b]+42

[a] Standard ink is similar to this formula, excepting that 12.5 g of dilute U. S. P. hydrochloric acid is substituted for tartaric acid, and 3.5 g of dye and 1 g of phenol are added.
[b] +=test was stopped before sediment appeared.

F. F. Rupert [6] found that inks containing gallic acid without tannic acid had a very low permanence when exposed to the weather. In the present work the relative permanence of the standard ink, which is essentially a tannic acid ink, and of inks containing only gallic acid was tested by exposing stripes in a Fade-Ometer for 150 hours. Both types of ink seemed to have the same degree of permanence.

2. IRON SALT

Ferrous sulphate is probably the only ferrous salt used in the preparation of ink. The pure heptahydrate is not hygroscopic, and it does not oxidize readily in air. These properties indicate the possibility of using this material for the preparation of ink powders. The ferrous sulphate used in this work was freed from ferric compounds by precipitation with alcohol.[7]

[5] Cir. BS C400, 7 (1933).
[6] Ind. Eng. Chem. 15, 489 (1923).
[7] E. Thorpe, Dictionary of Applied Chemistry 3, 681. (Longmans, Green & Co., London, 1922).

Ferric salts have also been used in inks. The effect of substituting an equivalent amount of ferric sulphate for ferrous sulphate is shown by comparing the corrosiveness of inks 9 and 10 in table 2. Since it is known that the dye has no corrosive effect, the increase in corrosiveness is due to the use of ferric sulphate. Apparently it is immaterial which ferric salt is used. Inks prepared respectively with ferric chloride, ferric chlorosulphate, or ferric sulphate showed no marked differences in keeping qualities or corrosion of steel pens. B. Walther [8] published several formulas for inks containing ferric chlorosulphate hexahydrate, a patented salt which is not hygroscopic. This salt was most successfully prepared by oxidixing an aqueous solution of ferrous sulphate with chlorine gas. The product contained less water than the hexahydrate, but in other respects the analysis checked with the theoretical formula.

Ferric sulphate was used to prepare the ferric inks because this material is not as hygroscopic as ferric chloride and it can be obtained more readily than ferric chlorosulphate. Since the ordinary reagent grade of ferric sulphate is not anhydrous, the material was analyzed for iron, and a sufficient quantity to give the desired amount of iron was used.

In the preparation of ink powders, materials that do not take up sufficient water to cause the prepared powder to form a cake are desired. In order to determine the behavior of those iron salts which seemed likely to fulfill this requirement, three powders were prepared, using ferrous sulphate crystals in the first, ferric sulphate in the second, and ferric chlorosulphate in the third. These powders were put in open test tubes and kept in an atmosphere of 50 percent relative humidity. The powder containing ferric chlorosulphate began to form a cake after 1 month, whereas the other two were still loose after 2 months. With moderate protection from atmospheric moisture, either ferrous sulphate crystals or anhydrous ferric sulphate is suitable for making ink powders.

3. STABILIZING AGENT

Inks contain acids to improve their keeping qualities. In general the acid prevents the formation of the basic iron salt, which is more readily oxidized than the normal compound. J. W. McBain [9] points out that sulphuric acid tends to improve the stability of ferrous sulphate solutions, whereas hydrochloric acid has the opposite effect on solutions of ferrous chloride. No information was given on the behavior of ferrous sulphate solutions containing hydrochloric acid, but it seems reasonable to believe that the behavior of this combination ought to be similar to that of the ferrous chloride solution containing hydrochloric acid. In an ink, the difference in the effect of hydrochloric and sulphuric acids is not noticeable, and for all practical purposes they may be interchanged, but from the above information it seems advisable to use sulphuric acid instead of hydrochloric acid. Tartaric, citric, and succinic acids were also used as stabilizing agents, and the resulting inks had practically the same keeping qualities as the standard ink. Of these three, tartaric acid was preferred because it is cheaper than the others. Oxalic acid cannot be used in inks containing ferrous salts because it precipitates

[8] Chem.-Ztg. 45, 842 (1921).
[9] J. Phys. Chem. 5, 623 (1901).

the iron as ferrous oxalate. This acid can, however, be used with ferric salts. Walther's formulas for inks containing ferric chlorosulphate require oxalic acid.

The amount of acid used in the standard writing ink was originally the result of a compromise between stability and corrosion of steel pens. Since the keeping quality of an ink is increased by replacing the tannic acid with gallic, the amount of stabilizing acid can be decreased, and the resulting ink will be less corrosive to steel pens. The amount of hydrochloric acid in the standard ink is chemically equivalent to 2.58 g of tartaric acid or 2.16 g of crystallized oxalic acid. Since solid materials are necessary in the preparation of ink powders, these two acids were used as stabilizing agents instead of hydrochloric acid or sulphuric acid. The amount of tartaric acid necessary to stabilize a ferrous ink that contains only gallic acid is shown in table 2 by comparing the results of tests made on inks 7, 8, and 9. Only a little over one-third as much acid as the standard ink contains is necessary, and the resulting ink is less corrosive to steel pens.

TABLE 2.—*Effect of acid content on corrosion and stability*

Ink no.	Composition in grams per liter of water						Corrosion of steel pens in mg dissolved	Stability in approximate days for sediment to form
	Gallic acid	Ferrous sulphate $FeSO_4 \cdot 7H_2O$	Ferric sulphate anhydrous	Oxalic acid	Tartaric acid	Dye		
7	10	15			2	3.5	35	[a] 60+
8	10	15			1	3.5	24	60+
9	10	15			0	3.5	20	7
10	10		10.7	0			62	4
11	10		10.7	1			46	18
12	10		10.7	1.5			28	18
13	10		10.7	2			23	21
14	10		10.7	2.5			16	25
15	10		10.7	3			10	42+

[a] +=tests were stopped before sediment appeared.

Oxalic acid is used as a stabilizing agent in inks made with ferric salts because in addition to preventing the formation of sediment, this acid retards the corrosion of steel pens by forming a protective coating of ferrous oxalate on them. Other acids, such as tartaric, hydrochloric, or sulphuric, will not do this. The results of the corrosion tests for inks 11 to 15, inclusive, show the effect of varying the concentration of oxalic acid. The corrosion of steel pens decreases with increasing concentration of oxalic acid.

The results given in a previous publication [10] show that inks made with oxalic acid have a marked deleterious effect on the aging of paper. Therefore, this type of ink is unfit for use in making permanent records.

4. PRESERVATIVE AND DYE

No experimental work was done on the use of a preservative to prevent mold growth on ink. Preservatives were not used in the experimental inks, and although the corks in the bottles became moldy, the inks were not affected.

[10] J. Research NBS 14, 463 (1935) RP779.

No attempt was made to change the dye ordinarily used in preparing the standard ink. It was noted, however, that this dye seemed to retain its brilliance when used in inks that did not contain chlorides. In the standard ink, the color is likely to fade toward a greenish shade. Perhaps this is the color change found by Walther when he prepared inks containing ferric chloride.

III. CONCLUSION

Formulas for ink, either liquid or powder, can be readily worked out from the data given here. Three such formulas are given in table 3.

TABLE 3.

Ingredient	Ink		
	16	17	18
Gallic acid	10.0 g	10.0 g	10.0 g.
Ferric sulphate, anhydrous	10.7 g		
Ferrous sulphate, $FeSO_4 \cdot 7H_2O$		15.0 g	15.0 g.
Oxalic acid	2.0 g		
Tartaric acid		1.0 g	
Sulphuric acid [a]			0.654 g.
Soluble blue (C. I. 707)	3.5 g	3.5 g	3.5 g.
Water to make	1 liter	1 liter	1 liter.

[a] Calculated as anhydrous H_2SO_4.

Inks 16 and 17 can be prepared as powders which, when dissolved in the proper amount of water, will produce ink that will comply with the requirements of Federal Specification TT–I–563, Ink; Writing. Ink 18 embodies the same characteristics as ink 17, except that it cannot be prepared in powdered form. To make a gallon of ink, the figures in the table must be multiplied by 3.79. These three inks are more stable and less corrosive to steel pens than the standard ink. Of these three inks, ink 16 is inferior to inks 17 and 18 because it has a lower stability and it contains oxalic acid, which attacks paper readily and tends to form a crust on steel pens. The stability of inks 17 and 18 makes them particularly suitable for use in fountain pens.

WASHINGTON, May 10, 1935.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP808

Part of Journal of Research of the National Bureau of Standards, Volume 15, July 1935

SEPARATION OF A DIMETHYLCYCLOHEXANE FRACTION FROM A MIDCONTINENT PETROLEUM [1]

By Robert T. Leslie [2]

ABSTRACT

A practically constant-boiling and constant-freezing material with an empirical formula of a monocyclic naphthene hydrocarbon was isolated from a fraction of a midcontinent petroleum boiling at approximately 119 to 121° C. For the purpose of identifying the material derived from petroleum, pure *m*- and *p*-xylene were hydrogenated and the constituents of the resulting mixtures were partially separated (probably *cis*- and *trans*- forms of the corresponding naphthenes) by fractional crystallization. The change of the refractive indices and freezing points of the hydrogenated products on repeated fractional crystallizations indicated that the naphthene from petroleum was probably chiefly *m*-dimethylcyclohexane. The infrared spectrogram of the product from petroleum showed a similarity to the spectrograms of both hydrogenated *m*- and *p*-xylenes

Photomicrographs showed distinct eutectic structures with excesses of one crystalline form in both synthetic products. The material from petroleum showed the presence of at least two crystalline forms, one of which melted at a higher temperature than the other. The cooling curves also indicated the presence of more than one crystal form. It is possible that the material isolated was a eutectic of isomers with a slight excess of one.

It is estimated that the octonaphthene was present in the original crude oil to the extent of not less than 0.15 percent by volume.

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I. INTRODUCTION

Analyses of petroleum by distillation generally indicate the presence of a considerable quantity of material boiling between 116 and 121° C. This is not surprising in view of the fact that the boiling points of at least four isomeric octanes, cycloheptane, and the *cis*- and *trans*- forms of two dimethylcyclohexanes are reported to lie

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

[2] Research Associate at the National Bureau of Standards representing the American Petroleum Institute.

within this range. The general nature of the constituents of this fraction of petroleum has been indicated by a number of investigators. Thus, Beilstein and Kurbatow[3] demonstrated the presence of both cyclic and paraffin series in American petroleum distillates of this boiling range by the action of nitric acid on the material. Evidence advanced by a number of investigators to show the presence of isomeric octanes, cycloheptane, and the dimethylcyclohexanes in oils from various sources is cited by Engler and Höfer.[4] Mabery,[5] working on Ohio, and Warren,[6] on Pennsylvania oils, found that the molecular weight of the fractions boiling at about 118 to 120° C. corresponded closely to octane hydrocarbons, but the carbon-hydrogen ratio showed the presence of a small amount of compounds with less hydrogen than is required for paraffins.

The actual identification of these compounds by comparison of their physical constants with those of synthetic materials is somewhat uncertain because of the contradictory values for the constants to be found in the literature. The confused state of these data is doubtless caused by the difficulty of preparing the pure synthetic compounds. Previous investigators have generally preferred to classify the compounds in this fraction of petroleum as isooctanes and octonaphthenes, and to base their opinions as to structure on the similarity of the petroleum fractions and impure synthetic materials, as indicated by their chemical behavior.

The object of the present work has been to isolate the material from petroleum in as pure condition as possible and to identify it tentatively, leaving the conclusions open to revision when subsequent investigations on the structure and properties of the synthetic substances make this possible.

The determination of the naphthene-hydrocarbon content of petroleum is of interest because of the part which these compounds play in the "knocking" characteristics of gasoline and the lubricating qualities of higher-boiling fractions. It appears also that there is much to be learned about the chemistry and the physical properties of this class of compounds. The fact that they resemble the paraffin hydrocarbons in their chemical inertness and knocking behavior in internal-combustion engines, but can be more or less readily dehydrogenated to aromatic hydrocarbons with quite different properties in these respects, makes their investigation important.

II. HISTORY OF THE MATERIAL AND INDICATIONS OF THE PRESENCE OF NAPHTHENES

The unshaded line C in the lower chart of figure 1 is the distillation curve between 100 and 129° C of the midcontinent oil[7] upon which the work of Project 6 of the American Petroleum Institute has concentrated, before the isolation of any material. This distribution resulted after an initial distillation in a refinery and four systematic fractional distillations in the laboratory. The shaded line D in the same chart shows the distribution of volumes after the removal of

[3] F. Beilstein and A. Kurbatow, Ber. deut. chem. Ges. **13**, 2028 (1880).
[4] C. Engler and H. v. Höfer. Die Chemie und Physik des Erdöls, S. Hirzel, Leipzig (1913).
[5] C. F. Mabery, Proc. Am. Acad. Sci. **31**, 1 (1895).
[6] C. M. Warren, Proc. Am. Acad. Sci. **27**, 78 (1891).
[7] Taken from well no. 6 of the South Ponca Field, Kay County, Okla.

toluene [8] from the material boiling below 110°, 2-methylheptane [9] boiling at 116 to 117°, and *n*-octane [10] at 123 to 126° C. It is to be observed that the original mountainous concentration of material boiling between 119 and 127° has been separated into two peaks by the removal of a large quantity of *n*-octane by crystallization and subsequent fractional distillations. Curve A, in the upper part of figure 1, shows the change in the refractive index with the boiling point of the fractions shown in curve D. Since the material was free from aromatic hydrocarbons, the abrupt rise in this curve between

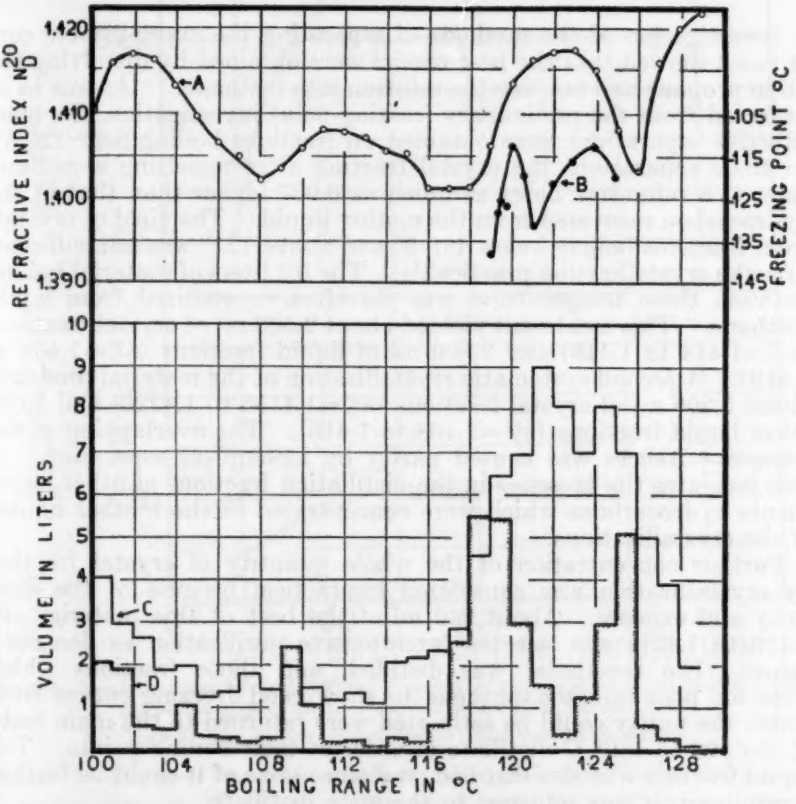

FIGURE 1.—*Volumes and properties of distillation fractions boiling between 100 and 129° C.*

A, Refractive indices; B, initial freezing halts; C, volumes before removal of any constituents; D, volumes after removal of toluene, isooctane, and *n*-octane and fifteen subsequent fractional distillations.

120 and 123° indicated the probable presence of naphthenic compounds, as suspected by other investigators. Before the removal of the *n*-octane and 2-methylheptane there was no indication of the presence of a component which was in sufficient concentration to crystallize. When the status of separation depicted by curve D was reached, however, freezing halts in the cooling curves of some of the samples became detectable. Curve B, figure 1, shows the tempera-

[8] J. H. Bruun, R. T. Leslie, and S. T. Schicktanz, BS J. Research **6**, 377 (1931) RP280.
[9] R. T. Leslie, BS J. Research **10**, 609 (1933) RP552.
[10] R. T. Leslie and S. T. Schicktanz, BS J. Research **6**, 377 (1931) RP282.

ture of the initial observed halts in the cooling curves of samples selected at intervals over the boiling range from which crystals could be obtained. It is apparent that the maximum concentration of crystallizable material occurred at approximately 120.5° C. Even at this temperature the concentration was small, as indicated by the low congealing temperature compared with the freezing points of the naphthenic compounds reported in this boiling range.

III. SEPARATION OF OCTONAPHTHENE FROM PETROLEUM

Investigation of the methods of separating the crystallizable constituent showed that the best results were obtained by dissolving the oil in propane and pouring the solution into methane.[11] As was to be expected from the preliminary freezing-point investigation, the most effective separations were obtained on fractions boiling near 120.5°. In these separations the crystal fraction after remelting sometimes showed a refractive index as much as 0.007 higher than that of the hydrocarbon recovered from the mother liquid. The yield of crystals from fractions boiling below 119.5° and above 121° was not sufficient to make crystallization practicable. The 5.5 liters of material boiling between these temperatures was therefore crystallized from liquid methane. This treatment yielded about 2,500 ml of crystal fractions (n_D^{20}=1.414 to 1.418) and 2,800 ml of liquid fractions (n_D^{20}=1.408 to 1.418). A second systematic crystallization of the material produced about 2,200 ml of crystal fractions (n_D^{20}=1.4155 to 1.4220) and 3,000 ml of liquid fractions (n_D^{20}=1.408 to 1.416). The overlapping of the refractive indices was caused partly by incomplete separation. It also indicates the presence in the distillation fractions of other naphthenic hydrocarbons which were concentrated in the mother liquids of the crystallizations.

Further concentration of the whole quantity of crystal fraction by crystallization was considered impractical because of the difficulty and expense. About 330 ml of the best of this material (n_D^{20} 1.420 to 1.421) was selected for intensive purification as described below. The remainder was distilled, and those fractions which were too poor in octonaphthene to show good freezing curves from which the purity could be estimated were returned to the main body of the 100 to 130° C distillate in order of their boiling points. The liquid fraction was also distilled, and since none of it could be further crystallized, it was returned to the main distillate.

The 330 ml of best material was carefully distilled through a spiral carborundum-coated column.[12] The results of this distillation are shown in figure 2. Fractions amounting to about 75 percent distilled within 0.2° C. The middle fractions amounting to 60 percent showed practically constant boiling points, refractive indices, and freezing points. This constant-distilling material was further purified by two crystallizations from methane and two without solvents. The last crystallization raised the freezing point by about 0.1° and caused little improvement in the shape of the curve. The cooling curve of the best sample is shown in figure 3, and its properties are given in table 1, together with those of the other concentrated material.

[11] R. T. Leslie, BS J. Research, 10, 609 (1933) RP552.
[12] Designed by S. T. Schicktanz.

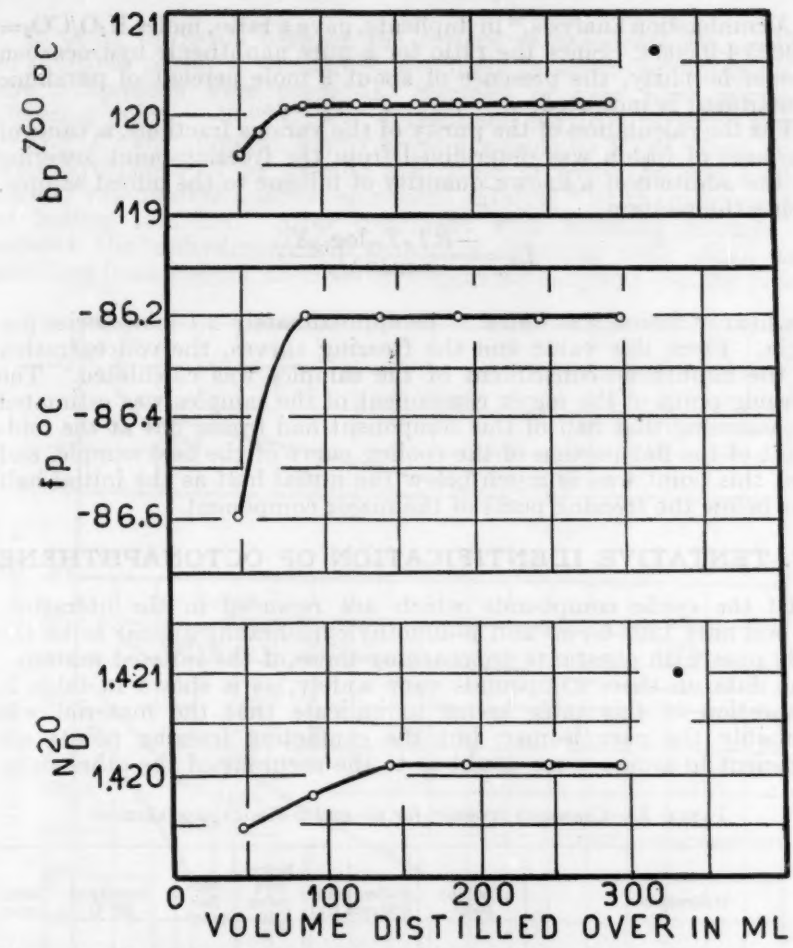

FIGURE 2.—*Properties of best 330-ml fraction of octonaphthene crystallized from petroleum after a distillation, but before final purification.*

The solid disks represent properties of the residue from the distillation.

TABLE 1.—*Physical properties of dimethylcyclohexane fractions from petroleum*

Lot	Volume	Freezing point [b]	Boiling point [c] (760 mm Hg)	Refractive index n_D^{20}	Concentration
	ml	*Degrees C*	*Degrees C*		*Mole percent*
I [a]	48	−84.8$_8$	120.0	1.4199$_8$	98.5
II	100	−86.4	119.9	1.4198	94.7
III	55	−87.0	119.8	1.4190	92.9
IV	420	−88.5	119.8	1.4162	88.7
V	125	−89.0	119.8	1.4167	87.3
VI	175	−92.4	119.6	1.4143	78.2
VII	230	−92.8	119.5	1.4131	77.2
VIII	100	−95.8	119.1	1.4120	69.8
IX	230	−96.0	120.0	1.4180	69.3
X	100	−97.0	119.8	1.4187	66.6

[a] The density of lot I, as determined by the Weights and Measures Division of the National Bureau of Standards, was 0.76492 ±0.00002 g/ml at 20° C.

[b] Value for lot I is the initial extrapolated freezing point. The values for the other lots are the initial observed points.

[c] The boiling points were determined in a Cottrell boiling-point apparatus.

A combustion analysis,[13] in duplicate, gave a ratio, moles $H_2O/CO_2=1.0025\pm0.0008$. Since the ratio for a pure naphthenic hydrocarbon should be unity, the presence of about 2 mole percent of paraffinic constituent is indicated.

For the calculation of the purity of the various fractions, a value of the heat of fusion was determined from the freezing-point lowering on the addition of a known quantity of toluene to the purest sample. Using the relation,

$$L_F=\frac{-RT_FT_{F0}\log_{10}X}{0.4343\Delta t_F},$$

the heat of fusion was found to be approximately 2.1 kilocalories per mole. From this value and the freezing curves, the concentration of the naphthene constituent of the samples was calculated. The freezing point of the major component of the samples was estimated by assuming that half of this component had frozen out at the mid-point of the flat portion of the cooling curve of the best sample, and that this point was as much below the initial halt as the initial halt was below the freezing point of the major component.

IV. TENTATIVE IDENTIFICATION OF OCTONAPHTHENE

Of the cyclic compounds which are reported in the literature, to boil near 120° C, *m*- and *p*-dimethylcyclohexane appear to be the only ones with constants approaching those of the isolated material. The data on these compounds vary widely, as is shown in table 2. Inspection of this table seems to indicate that the material was probably the para isomer, but the conflicting freezing points are sufficient to arouse some doubt as to the accuracy of the other data.

TABLE 2.—*Constants reported for m- and p-dimethylcyclohexane*

Hydrocarbon	Freezing point	Boiling point (760 mm Hg)	Refractive index n_D^{20}	Aniline point	Density at 20° C	Reference
	°C	°C		°C	g/ml	
m-Dimethylcyclohexane	Below −75	121.6±1	1.4255	47.8	[a] 0.7723[20/4]	1
cis-m-Dimethylcyclohexane	Below −75	121.0	1.4238		[a] .7735[20 vac]	2
trans-m-Dimethylcyclohexane		119[760]	1.4226			2
m-Dimethylcyclohexane		120[741]	1.4234		[a] .7736[18/4]	3
Do	−85	123.7	1.425		.771	4
Do		120.9 to 122.5	1.4253		.774	5
p-Dimethylcyclohexane	−59	121.7±1	1.4253	47.8	.7727	1
cis-p-Dimethylcyclohexane		120.8[745]	1.4206		.7671	2
trans-p-Dimethylcyclohexane		119[760]	1.4183		.7655	2
p-Dimethylcyclohexane	−86	120.5	1.421		.769	4
Do		122 to 124	1.4271		.777	5

[a] Specific gravity.

1. E. H. Garner and E. B. Evans, J. Inst. Petroleum Tech. 18, 107, 751 (1932).
2. F. Eisenlohr, Fortsch. Chem. 18, 9, 521 (1925).
3. C. Engler and H. v. Höfer, Die Chemie und Physik des Erdöls.
4. Int. Critical Tables, I, p. 222 (1926).
5. F. K. Signaigo and P. L. Cramer, J. Am. Chem. Soc. 55, 3326 (1933).

[13] The author is indebted to J. D. White for this determination.

In order to decide between the various values, synthetic samples of sufficient purity to distinguish definitely between the properties of the compounds were prepared. Samples of very pure *m*-xylene (freezing point, −49.9° C; $n_D^{25.2}$, 1.4945) and *p*-xylene (freezing point, +13.3° C; $n_D^{25.2}$, 1.4931), kindly made available by F. W. Rose, Jr.,[14] were hydrogenated by passing a mixture of hydrogen and hydrocarbon vapors over a nickel-aluminum catalyst [15] at the temperature of boiling toluidine. After treatment with nitrating mixture to remove the unhydrogenated aromatics, washing with alkali and distilling from sodium, 55 ml of hydrogenated *m*-xylene (boiling point,

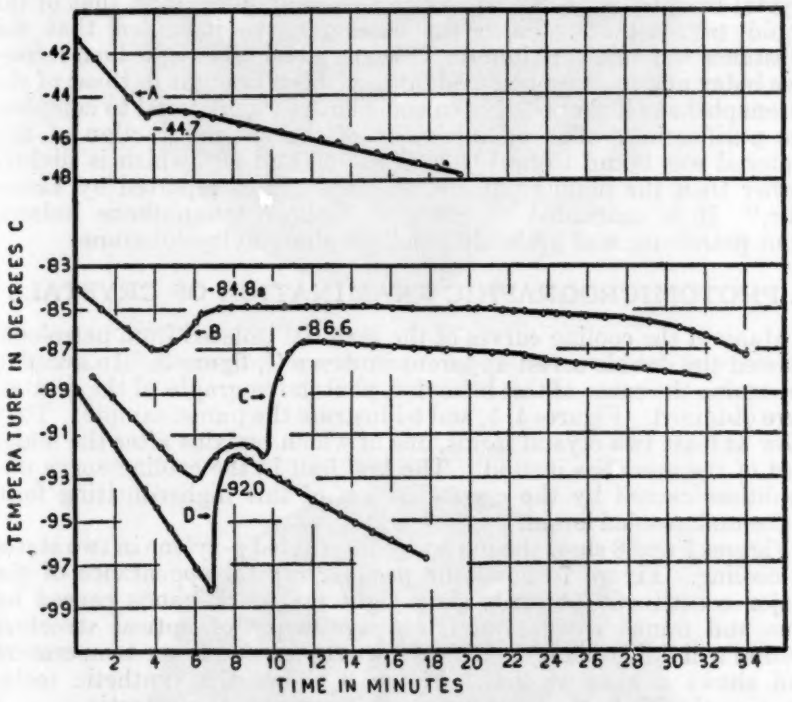

FIGURE 3.—*Cooling curves of hydrogenated m- and p-xylenes and of octonaphthene fractions from petroleum.*

A, Hydrogenated *p*-xylene; B, best sample from petroleum; C, mother liquid from crystallization of best sample; D, hydrogenated *m*-xylene.

121.3° C; n_D^{25}, 1.4230; freezing point, about −92.5) and 48 ml of hydrogenated *p*-xylene (boiling point, 121.3° C; n_D^{25}, 1.4220; eutectic halt, −94° C) were obtained. The cooling curves of both these samples indicated that they were far from pure substances. Evidently mixtures of *cis-* and *trans-* forms result on hydrogenation of these substances in the manner described.[16] The hydrogenated *p*-xylene was purified by a crystallization without the use of solvent, after which the cooling curve shown in figure 3 was obtained on the material. The initial freezing point (−44.7° C) is so high that the

[14] Prepared by the method of J. D. White and F. W. Rose, Jr., BS J. Research **9**, 711 (1932).
[15] N. Zelinsky and W. Kommarewsky, Ber. deut. chem. Ges. **57**, 667 (1924).
[16] G. Chavanne and E. Bode, J. Am. Chem. Soc. **52**, 1609 (1930).

particular stereoisomer of *p*-dimethylcyclohexane which was present in excess of the eutectic in the synthetic product cannot be identical with the major constituent of the isolated product. The other stereoisomer of *p*-dimethylcyclohexane is also eliminated by the fact that the refractive index of the mother liquid from the crystallization was too high (n_D^{25}, 1.4232, as compared to 1.4199_5 for the octonaphthene). The boiling point of the crystal fraction was found to be 121.0° C at 760 mm Hg.

The hydrogenated *m*-xylene was crystallized once without solvent and twice with methane. The final freezing curve (freezing point, about −92° C) is shown in figure 3. The final refractive index of the crystal fraction (n_D^{25}, 1.4228) was considerably lower than that of the liquid (n_D^{25}, 1.4232). Since the cooling curve indicated that the substance was still very impure, it seems possible that the final refractive index and freezing point might have been brought to those of the octonaphthene if there had been sufficient of the material to complete the purification. The boiling point of the crystal fraction of this material was found to be 121.3° C at 760 mm Hg, which is slightly higher than the boiling point of the *cis*-form as reported by Eisenlohr.[17] It is concluded therefore that the octonaphthene isolated from petroleum was probably chiefly *m*-dimethylcyclohexane.

V. PHOTOMICROGRAPHIC EXAMINATION OF CRYSTALS[18]

Many of the cooling curves of the material isolated from petroleum showed the double arrest apparent in curve C, figure 3. In order to determine the cause of this behavior, photomicrographs of the crystals were obtained. Figures 4, 5, and 6 illustrate the purest sample. They show at least two crystal forms, one of which remains after the major part of the mass has melted. The first halt in the cooling curve was doubtless caused by the crystallization of this higher-melting form in the undercooled liquid.

Figures 7 and 8 show the purest hydrogenated *p*-xylene in two states of cooling. Figure 7 shows the peculiar crystal appearance of the major constituent (crystals show light and dark bands caused by plus and minus elongation, i. e., asymmetry of optical structure around a dividing plane). Figure 8 was taken at a lower temperature and shows a eutectic mat. Figure 9 shows the synthetic meta-compound with both the excess constituent and the eutectic.

Comparison of the crystal forms of the synthetic samples with the best petroleum sample shows that all three products are alike in containing more than one crystal form. The angles and twinned structure of the higher-melting crystal form of the petroleum sample resemble those of the excess constituent which appears in the hydrogenated *p*-xylene.

To test the possibility that they were identical, some of the twinned crystals were isolated from the petroleum sample by cooling under the microscope and draining off the excess liquid. Hydrogenated *p*-xylene was then allowed to crystallize around them. On warming the

[17] F. Eisenlohr, Fortsch. Chem. Phys. Chem. **18**, 521 (1925).

[18] All photomicrographic work was done by C. P. Saylor. The photographs were made between crossed nicols and under a magnification of 71 ×. See W. H. Smith, C. P. Saylor, and H. J. Wing, B8 J. Research **10**, 479 (1933) RP544, for description of apparatus. For the work here described no acetone was used in the refrigerating dewar tube. The hydrocarbon was placed between small cover glasses in the bottom of the dewar tube in the optical path.

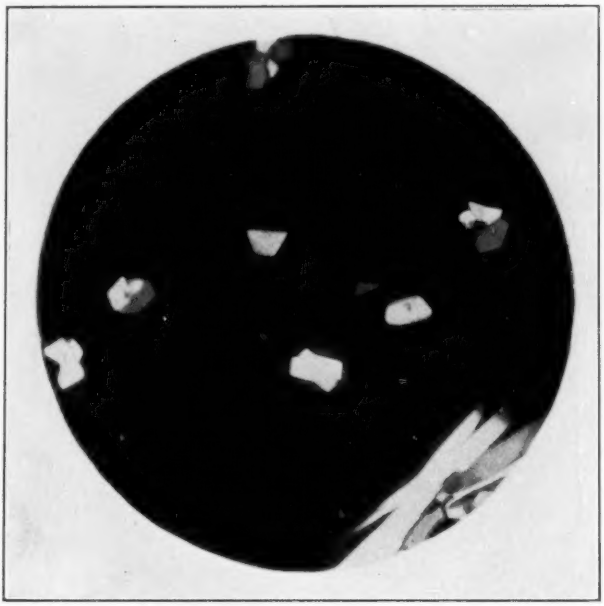

FIGURE 4.—*Best octonaphthene undercooled, warmed until only seeds remained, and cooled gradually.*

FIGURE 5.—*Same field shown in figure 4 on further gradual cooling.*

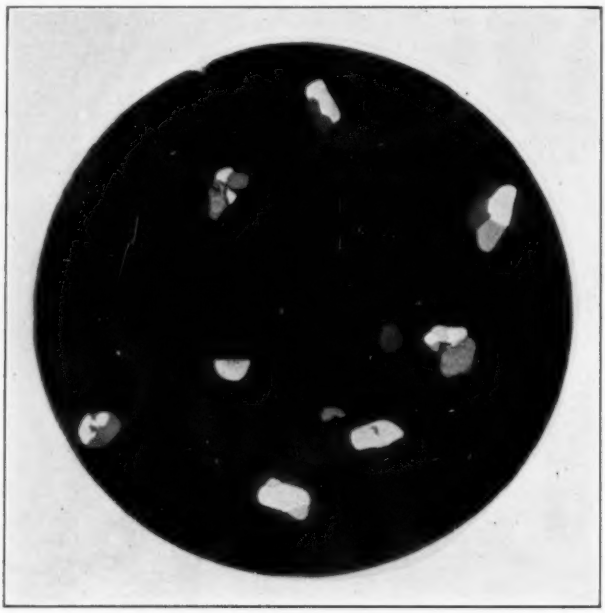

FIGURE 6.—*Field shown in figure 5 on gradual warming.*

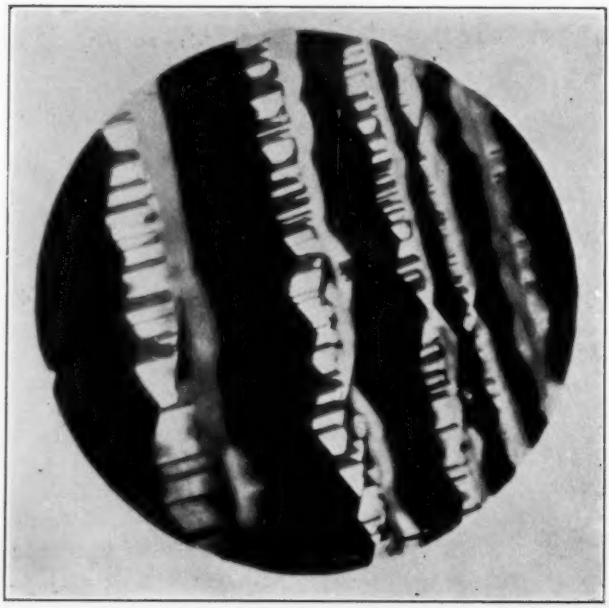

FIGURE 7.—*Hydrogenated p-xylene undercooled, warmed until only seeds remained, and cooled gradually to allow the first crystal phase to grow.*

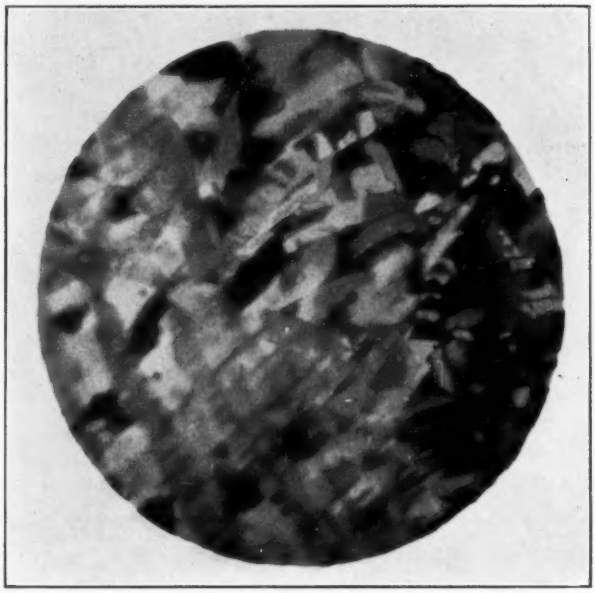

FIGURE 8.—*Same field shown in figure 7 on further gradual cooling.*

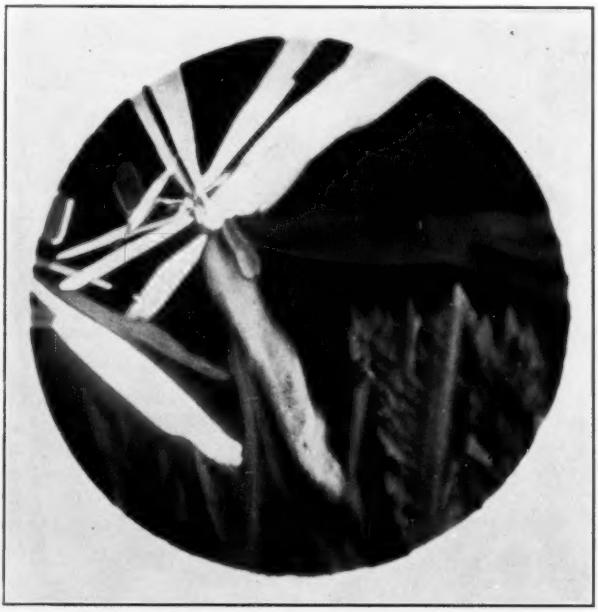

FIGURE 9.—*Hydrogenated m-xylene on gradual cooling.*
Both eutectic and excess constituent visible.

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mass, the twinned crystals seemed to disappear before the remainder. This behavior indicated that the twinned crystals appearing in the petroleum sample were not the higher-melting crystal constituent from the synthetic *p*-dimethylcyclohexane. Additional evidence for this conclusion was obtained by growing crystals from the synthetic *p*-compound, draining off the excess liquid, and adding octonaphthene which was undercooled below the melting point of its twinned crystals. The crystals dissolved, which showed that they were not in equilibrium with the octonaphthene.

Crystals of the higher-melting material from the synthetic meta-compound, obtained by drawing off the mother liquid as described above, remained in equilibrium with the cold octonaphthene. The presence of the seed crystals from the synthetic product also appeared

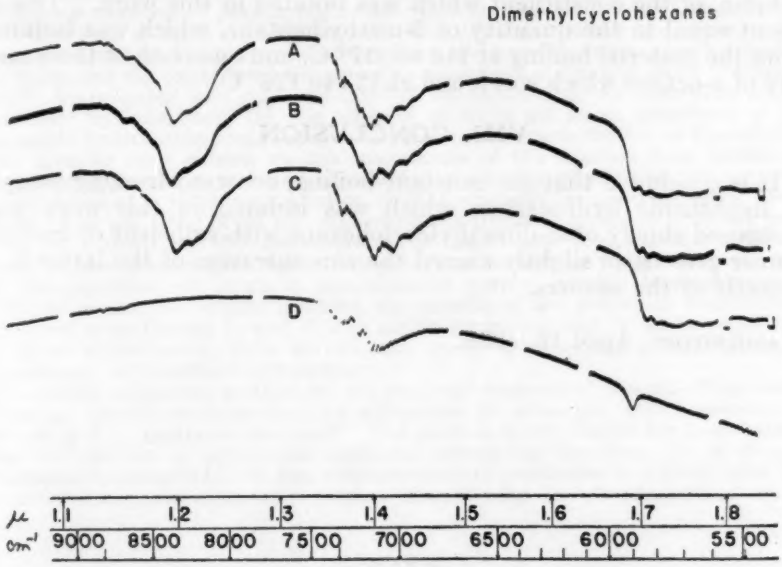

FIGURE 10.—*Infrared-absorption curves of dimethylcyclohexanes.*

Record of the transmission in the near infrared through 10 cm of solution of synthetic samples of dimethylcyclohexane and of the octonaphthene from petroleum in purified carbon tetrachloride. The concentrations were 0.0609, 0.0590, and 0.0589 molal for curves A, B, and C, respectively.
A, Hydrogenated *m*-xylene; *B*, octonaphthene fraction from petroleum; C, hydrogenated *p*-xylene; D, carbon tetrachloride.

to decrease the proportion of twinned crystals which formed. From the last experiment it appears that the lower-melting constituent in the octonaphthene from petroleum was identical with the higher-melting crystal constituent in the hydrogenated *m*-xylene.

VI. INFRARED-ABSORPTION SPECTRA OF DIMETHYLCYCLOHEXANES [19]

Comparison, figure 10, of the infrared-absorption spectrograms of the hydrogenated *p*- and *m*-xylene with that of the material isolated from petroleum shows that the latter is probably composed of deriva-

[19] The author is indebted to U. Liddel and O. R. Wulf, of the U. S. Bureau of Chemistry and Soils, for recording these spectrograms and interpreting the results.

tives of cyclohexane. Inspection also shows that the spectrogram of the naphthene from petroleum more nearly resembles that of hydrogenated *m*-xylene than that of the *p*-xylene, but is not identical with either. This lends further credence to the belief that the material was chiefly *m*-dimethylcyclohexane with some other constituent or more than one isomeric form present.

VII. ESTIMATION OF THE QUANTITY OF THE DIMETHYLCYCLOHEXANE FRACTION IN THE CRUDE PETROLEUM

In the approximately 2,200 liters of the original crude oil it is estimated that there were at least 3 liters, or about 0.15 percent by volume, of the constituent which was isolated in this work. This is about equal to the quantity of 2-methylheptane, which was isolated from the material boiling at 116 to 117° C, and one-sixth of the quantity of *n*-octane which was found at 123 to 126° C.

VIII. CONCLUSION

It is concluded that the constant-boiling, constant-freezing sample of naphthenic hydrocarbon which was isolated in this work was composed chiefly of *m*-dimethylcyclohexane with sufficient of another isomer present to slightly exceed the concentration of the latter in a eutectic of the isomers.

WASHINGTON, April 16, 1935.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP809

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SEPARATION OF PETROLEUM HYDROCARBONS WITH SILICA GEL [1]

By Beveridge J. Mair and Joseph D. White [2]

ABSTRACT

The fractionation, by filtration through columns of silica gel, of a number of binary mixtures of pure hydrocarbons boiling from 80 to 175° C is reported.

The results of these experiments show that (a) the aromatic and olefin hydrocarbons could be completely removed from the paraffin and naphthene hydrocarbons, but the capacity of the gel as an adsorbent of the one olefin ("diamylene") investigated was only one-third of its capacity as an adsorbent of the aromatic hydrocarbons; (b) the capacity of silica gel as an adsorbent of the aromatic hydrocarbons was found to depend on the concentration of the solution and also, to some extent, on the components of the solution from which the aromatic hydrocarbon is being adsorbed, the amount of *o*-xylene, for example, adsorbed from a 10 percent solution of that aromatic in *n*-nonane being about 12 to 13 ml per 100 g of gel and approximately the same for gel of different grain size; (c) a small but definite separation of naphthene from paraffin hydrocarbons occurred, the naphthenes tending to be adsorbed by the gel in preference to the paraffins; (d) a slight separation of normal paraffin hydrocarbons of different molecular weights occurred, the paraffin of low molecular weight being adsorbed in preference to that of high molecular weight; and (e) under conditions of these experiments, silica gel did not crack or otherwise attack aromatic, naphthene, or paraffin hydrocarbons.

A simple laboratory method for the complete removal of aromatic from naphthene or paraffin hydrocarbons by adsorption on silica gel, with a recovery of 98 percent or better, is described. The method is very useful for investigating the composition of petroleum distillates containing less than 15 percent of aromatic hydrocarbon. If the concentration of aromatics is higher than this a preliminary extraction with sulphur dioxide may be advantageous.

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[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

[2] Research Associates at the National Bureau of Standards representing the American Petroleum Institute.

I. INTRODUCTION

In an investigation in progress at this Bureau on the isolation, identification, and determination of the hydrocarbons in petroleum, a simple method by which the aromatics may be separated completely from the naphthenes and paraffins is needed. The method should preferably be a physical one, and should permit nearly quantitative recovery of unchanged hydrocarbons.

Extraction with liquid sulphur dioxide at low temperatures may be employed to advantage with fractions rich in aromatics, but the complete removal of aromatic hydrocarbons by this solvent is not practical. Two chemical methods, nitration or sulphonation, may also be used for removal of aromatics. With nitration the aromatics cannot easily be regenerated, while with sulphonation the aromatics can usually be recovered by hydrolysis of the sulphonic acids. Both methods involve the use of a strong oxidizing agent for a considerable period of time, and there is consequently danger that any nonaromatic hydrocarbons present may also be attacked. With these methods it is difficult to remove completely the last trace of nitro compounds or sulphonic acids from the unattacked oil.

The use of adsorbents in petroleum refining for the removal of compounds containing sulphur and oxygen and of hydrocarbons with a low ratio of hydrogen to carbon is well known. Most investigations on the separation by adsorbents of the hydrocarbons in petroleum have been made with such complex mixtures that little definite information is available. Day and coworkers (1)[3] in 1911 found that when a solution of benzene and a paraffin oil is allowed to diffuse upward through a tube packed with fuller's earth, the benzene tends to collect in the lower sections and the paraffin oil in the upper sections of the tube. Tarasov (2) in 1927 reported that all the aromatics could be removed from the naphthenes and paraffins by adsorption if sufficient silica gel was used. More recently, Hofmeier and Meiner (3) studied the action of five silica gels on the naphtha fraction of petroleum and found that with the best gel the aromatic content could be reduced by only 50 percent. Neither of these investigators found any separation of paraffins and naphthenes. Hofmeier and Meiner did not obtain a satisfactory recovery of oil.

In this paper are presented the results of experiments on the adsorption by silica gel of binary mixtures of hydrocarbons of different types and molecular weights. In particular, a simple method is described which should find extensive use in removing aromatic hydrocarbons from petroleum distillates. This method is considered superior to nitration or sulphonation in simplicity, completeness of removal of aromatics, and total recovery of oil. It is superior to extraction with sulphur dioxide in simplicity and completeness of removal. The method is scarcely practical for mixtures containing more than 15 percent of aromatics because of the small volume of aromatic-free oil recovered from such concentrated mixtures. In this case a preliminary extraction with sulphur dioxide is recommended.

II. APPARATUS AND MATERIALS

The apparatus is very simple, consisting of glass tubes mounted vertically and filled with silica gel. One of these tubes is shown in

[3] The figures in parentheses throughout this paper refer to the numbered references listed on page 62.

figure 1. At the top is sealed a glass bulb as a reservoir for the hydrocarbon mixture. To the top of this reservoir may be attached a rubber tube through which air pressure can be applied during filtration. At the bottom of the adsorption tube is sealed a smaller tube which extends into a stoppered graduated cylinder. A small plug of glass cotton at the bottom of the adsorption tube suffices to hold the silica gel in place. The adsorption tubes used in these experiments were 40 cm long and had an inside diameter of 1.5 to 1.7 cm.

Two grades of silica gel obtained from the Silica Gel Corporation, Baltimore, Md., were used. These were grade "150–F–850" (40- to 200-mesh) and "Intermediate" (200-mesh and finer). These grades will be referred to throughout the rest of this paper as coarse and fine, respectively. The gel, after use and after displacement of the oil with water, was reactivated by transferring it while wet to a Pyrex-glass tube, sucking it as dry as possible and placing it in an oven, where it was heated for 24 hours at a temperature of 300 to 350° C, while air was aspirated through it. Both the original gel and the reactivated gel were stored in moistureproof containers.

All the hydrocarbons used in this work, except those mentioned below, were isolated from petroleum, or prepared synthetically or purified in this laboratory. The samples were not of the highest purity, but they were sufficiently pure for the purpose of these experiments. Their refractive indices differed by only a few units in the fourth decimal place from those of the best material prepared by us. The *n*-heptane of Jeffrey pine origin and the 2,2,4-trimethylpentane were commercial materials of high purity. The *n*-tetradecane was an Eastman product. Its treatment before use is described in a later section of this paper. The diamylene was a mixture of 3,5,5-trimethylheptene-2 and 3,4,5,5-tetramethylhexene-2. This sample was obtained through the courtesy of W. L. Drake (4), who has described the analysis of the mixture.

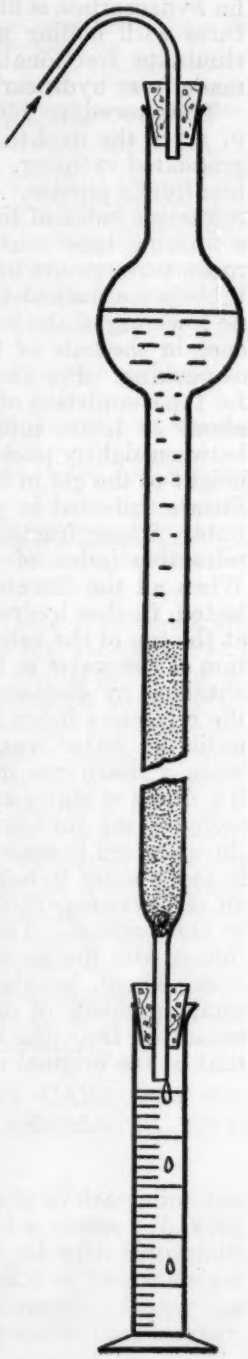

FIGURE 1.—*Adsorption tube.*

III. ADSORPTION EXPERIMENTS WITH MIXTURES OF AN AROMATIC AND A NAPHTHENE OR A PARAFFIN HYDROCARBON

These experiments were designed principally to show the degree of separation obtained when an aromatic hydrocarbon mixed with a naphthene or a paraf

fin hydrocarbon is filtered through silica gel. A series of binary mixtures with boiling points from about 80 to 175° C was used. To eliminate fractionation by evaporation, each binary mixture was made from hydrocarbons with approximately the same boiling point.

The procedure adopted for these experiments was to measure out 97 ml of the naphthene or paraffin hydrocarbon in a glass-stoppered graduated cylinder. To this was added 5 ml of aromatic hydrocarbon from a pipette. The cylinder was stoppered and shaken, and the refractive index of the mixture observed. It was then transferred to a filtering tube containing 50 g of fine gel and allowed to filter at room temperature under air pressure of about 4 lb/in^2. Some of the tubes were packed tightly with silica gel by tapping the tube until no lowering of the level of the gel could be observed. A great difference in the rate of filtration was noticed, depending on the degree of packing. For those packed tightly, about 48 hours was required for the completion of an experiment, while with those loosely packed, about 16 hours sufficed. No significant difference in effectiveness between tightly packed and loosely packed tubes was observed. The height of the gel in the tubes varied from 36 to 40 cm. Fractions of filtrate collected in graduated cylinders were removed from time to time. These fractions all had the same refractive index, i. e., the refractive index of the pure paraffin or naphthene used initially. When all the filtrate which would drain of its own accord had collected, further hydrocarbon fractions were displaced by adding water at the top of the tube. A sharp line of demarcation showed the position of the water in the tube. The refractive indices of the fractions obtained by displacement with water usually remained constant at the refractive index of the pure paraffin or naphthene in the mixture until the water reached about 3 cm from the bottom of the tube, when a sharp rise in the refractive index occurred. After the first few drops of water appeared in the graduated cylinder, filtration was stopped, the tube was disconnected, the bottom end stoppered, and the silica gel loosened with a reamer and transferred as a suspension in more water to a 500-ml erlenmeyer flask. During this treatment, an oil layer separated on top of the water and the silica gel settled to the bottom. The oil and water were poured into a separatory funnel, and the water run again onto the silica gel in the erlenmeyer flask, where, by vigorous shaking, it was possible to get a second small quantity of oil to separate. The refractive index of the oil separated from the silica gel in this manner was much higher than that of the original mixture.

TABLE 1.—*Data showing the separation of aromatic from naphthene or paraffin hydrocarbons by adsorption on 50 grams of fine silica gel*

Hydrocarbons	Volume of hydrocarbons	Refractive indices of		Volume and refractive indices of fractions after passage through silica gel								
		Hydrocarbons	Mixtures	Filtrate		Main portion of filtrate displaced by water		Last portion of filtrate displaced by water		Adsorbed material shaken out with water		Total volume recovered
	ml	n_D^{25}	n_D^{25}	ml	n_D^{25}	ml	n_D^{25}	ml	n_D^{25}	ml	n_D^{25}	ml
Mesitylene	5	1.4972	1.4139	62	1.4096	32.5	1.4096	3	1.4496	4.4	1.4683	101.9
n-Decane [1]	97	1.4098										
m-Xylene	5	1.4949	1.4000	63	1.3950	29.2	1.3950	3.5	1.4068	4.2	1.4677	99.9
n-Octane [1]	97	1.3952										
Toluene	5	1.4940	1.4237	61.7	1.4202	15.1	1.4202	3	1.4522	2.5	1.4687	99.3
Methylcyclohexane	97	1.4205				17	1.4225					
Benzene	5	1.4977	1.4105	65.5	1.4069	28	1.4094	3.5	1.4209	1.8	1.4610	98.8
Methylcyclopentane	97	1.4069										

[1] These hydrocarbons had refractive indices a little higher than the values obtained on the best samples isolated from petroleum in this laboratory. They evidently contained traces of aromatics or unsaturated hydrocarbons. After the mixture had run through silica gel, the values of the filtrate approached more nearly the values for the pure hydrocarbons.

The results of these experiments are shown in table 1, in which are tabulated the refractive indices and volumes of the starting material, the various fractions of filtrate, the filtrate displaced by water, and the adsorbed material shaken out of the silica gel with water. It is evident from the refractive index that the aromatic hydrocarbons were removed from the filtrate, and that in two cases (mesitylene with *n*-decane and *m*-xylene with *n*-octane) the first portion of the filtrate displaced by water was also free from them. For the other two cases, toluene with methylcyclohexane and benzene with methylcyclopentane, a rise in the refractive index of the filtrate displaced by water was noticed. This may have been due to allowing the water to come too close to the bottom of the tube before withdrawing the fraction, or to the fact that the gel had reached its capacity at this stage. The recovery for this series averaged about 98 percent. From an initial solution of 102 ml, made from 97 ml of a paraffin and 5 ml of an aromatic hydrocarbon, more than 90 ml of pure paraffin hydrocarbon and 5 to 8 ml of aromatic concentrate were obtained.

IV. EXPERIMENTS TO DETERMINE THE CAPACITY OF SILICA GEL AS AN ADSORBENT OF AROMATIC AND OLEFIN HYDROCARBONS

In table 2 are recorded the results of experiments to determine the capacity of a fine gel, a reactivated fine gel, and a coarse gel, with respect to aromatic hydrocarbons, and of a fine gel with respect to olefin hydrocarbons. When the saturation capacity of fine silica gel is reached, the refractive index of the filtrate rises rapidly, during the passage of a few milliliters, from that of the pure paraffin hydrocarbon to that of the mixture employed.

TABLE 2.—*Data showing the capacity of certain silica gels as adsorbents of aromatic and olefin hydrocarbons*

Gel		Hydrocarbons	Volume of hydrocarbon	Refractive indices of:		Volumes and refractive indices of fractions after passage through silica gel								Total volume recovered
						Filtrate [1]		Main portion of filtrate displaced by water		Last portion of filtrate displaced by water		Adsorbed material shaken out with water		
Wt.	Condition			Hydrocarbon	Mixtures									
			ml	n_D^{25}	n_D^{25}	ml	n_D^{25}	ml	n_D^{25}	ml	n_D^{25}	ml	n_D^{25}	ml
50	Fine	o-Xylene n-Nonane	10 92	1.5030 1.4039	1.4132	61.5 7.0	1.4039 1.4094	22.7	1.4132	4.0	1.4533	3.2	1.4922	98.4
50	do	o-Xylene n-Nonane	10 194	1.5030 1.4039	1.4084	99.8 7.2 4.0 54.5	1.4039 1.4040 1.4083 1.4084	24	1.4084	7.5	1.4197	6.8	1.4584	203.8
50	do	Toluene n-Heptane	10 92	1.4939 1.3850	1.3953	55.5 7.2	1.3850 1.3894	4.8 22	1.3950 1.3953	6.0	1.4207	4.7	1.4620	100.2
50	Fine, reactivated	o-Xylene n-Nonane	10 92	1.5030 1.4039	1.4132	55.3	1.4039	9.5 24	1.4061 1.4132	5.0	1.4390	6.4	1.4761	100.2
50	Coarse	o-Xylene n-Nonane	10 92	1.4039 1.5030	1.4132	45 12 12.6 4.0	1.4039 1.4049 1.4104 1.4124	9.5 8.0	1.4130 1.4131	4.0	1.4548	4.7	1.4828	99.8
50	Fine	Diamylene n-Decane	5 97	1.4330 1.4096	1.4107	40.5 14	1.4096 1.4105	31	1.4105	3.6 2.0	1.4108 1.4141	7.0	1.4146	98.3

[1] Small fractions of filtrate were removed from time to time. The total volume of those with the same refractive index is recorded here.

The capacity of silica gel as an adsorbent of aromatic hydrocarbons depends on the concentration of the solution and also to some extent on the components of the solution from which the aromatic hydrocarbon is being adsorbed. In the first experiment with fine gel, 61.5 ml of filtrate free from *o*-xylene was obtained and the *o*-xylene content of a further 7 ml was reduced by an amount corresponding to its complete removal from 2.9 ml. Thus, 50 g of fine gel was capable of adsorbing 6.4 ml of *o*-xylene from a 10-percent solution of that aromatic hydrocarbon in *n*-nonane. In the second experiment, in which a 5-percent solution of *o*-xylene in *n*-nonane was used, the *o*-xylene was removed from 107 ml, so that 50 g of fine gel adsorbed about 5.35 ml of *o*-xylene from a solution of this concentration. In experiment 3, the adsorption capacity of 50 g of fine gel with respect to a different aromatic hydrocarbon, namely toluene, is shown. In this case, 55.5 ml of filtrate free from toluene was obtained and the toluene content of a further 7.2 ml reduced by an amount corresponding to 4.1 ml, so that about 5.96 ml of toluene was adsorbed from a 10-percent solution of that aromatic hydrocarbon in *n*-heptane.

The reactivated fine gel is, within the limits of the experiments, as good as the original, because when used with a 10-percent solution of *o*-xylene in *n*-nonane, 55.3 ml of filtrate free from *o*-xylene was obtained and the *o*-xylene content of 9.5 ml was reduced by an amount corresponding to 7.2 ml. A 50-g portion of this gel therefore adsorbed about 6.3 ml of *o*-xylene. The coarse gel removed completely the *o*-xylene from only 45 ml, and the rise in the refractive index to that of the original mixture did not occur within so small a volume as with the fine gel. The capacity of the coarse gel does not seem to be much less than that of fine gel, about 6.0 ml of *o*-xylene being adsorbed from a 10-percent solution in *n*-nonane by 50 g of gel. Channeling was apparent with the coarse gel and probably accounts for the less effective separation. However, the speed of filtration is much more rapid than with the fine gel and so, for some purposes, it may be preferable. The experiment with diamylene and *n*-decane shows that

silica gel removed completely the olefin hydrocarbon from its mixture with a paraffin. For a solution containing 5 ml of diamylene and 97 ml of *n*-decane, 40.5 ml of filtrate was obtained free from the olefin hydrocarbon, when 50 g of gel was used. Thus, 50 g of gel adsorbed about 2 ml of diamylene, which volume is approximately one-third that of the aromatic which can be adsorbed by the same quantity of gel. This interesting fact may be associated with the number of double bonds in the molecule, *o*-xylene having three and diamylene one.

V. ADSORPTION EXPERIMENTS WITH MIXTURES OF A NAPHTHENE AND A PARAFFIN HYDROCARBON

These experiments were designed to show the separation obtained when a naphthene hydrocarbon mixed with a paraffin hydrocarbon is filtered through silica gel. As with the preceding experiments, each mixture was made from hydrocarbons with approximately the same boiling point. Naphthenes with both 5- and 6-membered rings and both normal and branched-chain paraffins were used. Since the presence of small traces of such an impurity as an aromatic or unsaturated hydrocarbon would render the results of these experiments unreliable, it was first established that the individual hydrocarbons did not fractionate when passed through silica gel. The results of the experiment are shown in table 3. A small but quite definite separation occurred in every case, the naphthene tending to be adsorbed by the gel. The first 6 ml of filtrate had a definitely lower refractive index than the original mixture, the first 1 or 2 ml having an index lower than the original by 2 to 3 parts in the third decimal place, which corresponds to a reduction of the naphthene content, from the original 10, to 2 or 3 percent. The adsorbed material had a definitely higher refractive index than the original. The separation is disappointingly small. Nevertheless, the separation of naphthenes from paraffins is frequently so difficult that a method which gives any separation whatsoever is worthy of consideration as a research tool.

TABLE 3.—*Data showing the separation of naphthene from paraffin or isoparaffin hydrocarbons by adsorption on 50 grams of fine silica gel*

Hydrocarbons	Volume of hydrocarbons	Refractive indices of:		Volume and refractive indices of fractions after passage through silica gel								
		Hydrocarbons	Mixtures	Filtrate [1]		Main portion of filtrate displaced by water		Last portion of filtrate displaced by water		Adsorbed material shaken out with water		Total volume recovered
	ml	n_D^{25}	n_D^{25}	ml	n_D^{25}	ml	n_D^{25}	ml	n_D^{25}	ml	n_D^{25}	ml
n-Heptane	92	1.3850	1.3885	1	1.3861	24.6	1.3886	----	----	7.6	1.3893	98.9
Methylcyclohexane	10	1.4202		3	1.3866							
				2	1.3879							
				60.7	1.3885							
2,2,4-trimethylpentane	92	1.3890	1.3922	2	1.3898	7	1.3922	1.5	1.3932	3.2	1.3930	100.9
Methylcyclohexane	10	1.4202		4	1.3910	24.7	1.3923					
				11.5	1.3921							
				47	1.3922							
n-Octane	50	1.3950	1.3980	1.5	1.3954	27.5	1.3980	----	----	8.5	1.3987	53.2
Nonanaphthene (a cyclopentane)	5	1.4273		2.2	1.3969							
				2.0	1.3978							
				11.5	1.3980							

[1] Small fractions of filtrate were removed from time to time. The total volume of those with the same refractive index is recorded here.

VI. AN ADSORPTION EXPERIMENT WITH A MIXTURE OF NORMAL PARAFFIN HYDROCARBONS OF DIFFERENT MOLECULAR WEIGHTS

This experiment was performed to determine whether any separation occurred when a mixture of normal paraffin hydrocarbons of different molecular weights was filtered through silica gel. To minimize fractionation by evaporation, hydrocarbons with relatively high boiling points (*n*-nonane and *n*-tetradecane) were chosen. The *n*-tetradecane was an Eastman product with refractive index $n_D^{25}=1.4270$. This material had an odor of cracked compounds so it was filtered twice through silica gel, and yielded a filtrate with refractive index $n_D^{25}=1.4266$. The *n*-nonane from petroleum was also given a preliminary filtration through silica gel. The results of these experiments are shown in table 4. The first 6 ml of filtrate is definitely higher in refractive index than the original mixture and the adsorbed material is definitely lower in refractive index. These results show that the hydrocarbon of low molecular weight was adsorbed in preference to that of high molecular weight. These results are in contrast to what is stated to happen with the lubricating oil fraction of petroleum in which, according to Kalichevesky and Stagner (5), paraffins of high molecular weight are more readily adsorbed than those of low molecular weight.

TABLE 4.—*Data showing the separation of normal paraffin hydrocarbons of different molecular weights by adsorption on 40 grams of fine silica gel*

Hydrocarbons	Volume of hydrocarbons	Refractive indices of:		Volume and refractive indices of fractions after passage through silica gel								
		Hydrocarbons	Mixtures	Filtrate [1]		Main portion of filtrate displaced by water		Last portion of filtrate displaced by water		Adsorbed material shaken out with water		Total volume recovered
	ml	n_D^{25}	n_D^{25}	ml	n_D^{25}	ml	n_D^{25}	ml	n_D^{25}	ml	n_D^{25}	ml
n-Tetradecane	25	1.4266	1.4156	1.5	1.4196	21.5	1.4158	4.0	1.4152	6.0	1.4124	47.8
n-Nonane	25	1.4039		2.3	1.4179							
				2.3	1.4158							
				10.2	1.4156							

[1] Small fractions of filtrate were removed from time to time. The total volume of those with the same refractive index is recorded here.

VII. EXPERIMENTS TO ASCERTAIN WHETHER SILICA GEL DECOMPOSES A MIXTURE OF HYDROCARBONS

Silica gel is believed to act as a cracking catalyst under certain conditions. Several experiments were performed to determine whether, under the conditions employed here, the gel had any deleterious effect on the oil. Since the filtrates were found to have the same refractive indices as the pure hydrocarbons, it is evident that the gel had no harmful effect on them. The composition of the adsorbed material was also tested. A volume of 8.5 ml of the adsorbed material ($n_D^{25}=1.4810$), from the previous experiments on the mixtures of *o*-xylene with *n*-nonane, was sulphonated with concen-

trated sulphuric acid. From this was obtained 1.8 ml of unattacked oil with refractive index $n_D^{25}=1.4043$, which is only slightly higher than that of *n*-nonane. The sulphonated material was then transferred to a flask for hydrolysis and steam passed through at 110° C. to remove any traces of unattacked oil. No measurable quantity was collected at this temperature. The temperature was then raised. Hydrolysis began at 155° C. From 155 to 165° C, 3.5 ml with the same refractive index as *o*-xylene ($n_D^{25}=1.5030$) was collected. From 165 to 170° C, 0.3 ml more was collected, with a refractive index $n_D^{25}=1.5038$.

The results show that *n*-nonane and *o*-xylene can be recovered unchanged from the adsorbed material rich in aromatics. Further evidence that silica gel has no harmful effect on these hydrocarbons was obtained from an experiment with a mixture of pseudocumene and *n*-decane in which the filtrate and the adsorbed material were carefully recombined. In this experiment, the filtrate was collected as one fraction in the graduated cylinder in which the hydrocarbons were mixed. Contrary to the usual practice of shaking the adsorbed material out of the silica gel with water in an erlenmeyer flask, the silica gel and adsorbed material were transferred directly to a distilling flask as a suspension in water and the adsorbed material was distilled over with steam. Its refractive index was then observed and it was recombined with the filtrate. The volumes and refractive indices of the original mixture, the filtrate, the adsorbed material, and the recombined fractions are shown in table 5. It can be seen that only 0.6 ml was lost in this procedure. The greater part of this loss probably occurred in the adsorbed material of high refractive index, which underwent more operations than the filtrate. The slightly lower refractive index of the recombined material (only 3 parts in the fourth decimal place) is attributable to the proportionately greater loss of adsorbed material. It is evident that no appreciable harm, if any, was done to the oil.

TABLE 5.—*Data of an experiment to ascertain whether silica gel decomposes a mixture of n-decane and pseudocumene*

Material	Volume	n_D^{25}
	ml	
Mixture	98	1.4182
Filtrate	88	1.4122
Adsorbed material steamed out of gel	9.4	1.4765
Recombined fractions	97.4	1.4179

VIII. APPLICATION OF SILICA GEL ADSORPTION TO THE FRACTIONATION OF A DISTILLATE OF PETROLEUM BOILING BETWEEN 140 AND 145.5° C

Adsorption on silica gel has been used in this laboratory to remove aromatic hydrocarbons from a 17-liter fraction of petroleum distillate boiling normally between 140 and 145.5° C. It consisted chiefly of a mixture of isononanes and some naphthenes, but it also contained a small amount of aromatic constitutents. The last named were originally present in large quantities, and although an interlocking process of extraction with liquid sulphur dioxide and fractional dis-

tillation had been used to remove the greater part of them (6), some still remained. In a final distillation the portion immiscible with sulphur dioxide had been separated into 0.5° C cuts. The material boiling near 140° C and near 145° C smelled faintly of aromatic hydrocarbons. Samples of these fractions also yielded upon nitration a small amount of nitro product in the form of a red oil. In the material boiling between 142 and 144° C, where the bulk of paraffin constituents had concentrated, only a little aromatic material could be detected. Nitration tests showed that the average aromatic content of the whole distillate was about 2 percent.

In addition to the constituents mentioned, the distillate contained some "cracked" material. After distillation, it had been stored in glass bottles for three years. When the present work was begun, it was observed to have deposited a thin ring of gum where the oil surface wet the bottle. Likewise, a film of sludge was observed at the bottom of the oil, notably in the bottles containing distillation residues. The residues were also consistently yellow in color and possessed an unpleasant odor. To ascertain if the color, odor, and gum could be removed by adsorption, a sample of residue was filtered through a column of silica gel. As more and more oil passed through the gel, the top layer became colored—at first a light amber, later an amber red. (This coloration likewise had been observed when the olefin, diamylene, was passed through gel.) Some of the coloration produced on the gel was attributed to the polymerization or oxidation of unsaturated hydrocarbons arising from the cracking of the oil during distillation. The filtered oil was colorless and had no unpleasant odor, which was taken to mean that gum had been removed completely by the gel. Once the gum was removed, the oil remained stable with further filtration as evidenced by the fact that no further coloration was produced.

To remove both aromatic hydrocarbons and gum from the distillate, it was filtered through silica gel in essentially the same manner as were the synthetic mixtures of hydrocarbons. Oil was recovered from the spent gel in a similar way.

In this operation, it was obvious that, since the capacity of the gel to adsorb aromatic hydrocarbons varied with their concentration in the oil being filtered, some aromatic material adsorbed from more concentrated solutions would be dislodged from the gel when oil with a lower aromatic concentration was filtered through. To prevent this occurring all of the distillate was blended, before filtering, into three fractions corresponding approximately to constant-boiling mixtures. These are listed in table 6 according to their boiling range.

TABLE 6.—*Volumes and refractive indices of fractions of petroleum distillate before and after filtering through silica gel*

Boiling range 760 mm before filtering	Volume				Refractive index		
	Before filtering	After filtering		Lost by filtering	Before filtering	After filtering	
		Filtrate	Adsorbed			Filtrate	Adsorbed
Degrees C	ml	ml	ml	ml	n_D^{25}	n_D^{25}	n_D^{25}
140 to 142.5	5,230	4,905	210	115	1.415	1.4125	1.445
142.5 to 144	5,850	5,380	360	110	1.4125	1.4115	1.425
144 to 145.5	5,660	5,150	460	50	1.418	1.416	1.438

In practice, coarse gel was used for the most part because of the decidedly shorter time required to filter 17 liters of oil. Although its effectiveness in removing aromatic constituents was somewhat less than that for fine gel, because of channeling, the difference was minimized by using columns no greater than 3 cm in diameter. When channeling had obviously occurred, the oil was refiltered through fresh columns of gel. The columns were about 50 cm long. One measuring 2 by 50 cm held about 100 g of gel; one measuring 3 by 50 cm held 200 g. The time required for oil to flow from top to bottom of the column, under a hydrostatic head of 10 cm of oil, was about 20 minutes. Longer columns were not used because it was more difficult to remove the gel.

The procedure adopted for the systematic filtration was as follows. A portion of the blended distillate was filtered through the columns of gel. Portions of filtrate were removed until the first rise in refractive index was observed and were stored as being free of aromatics. This procedure was followed since it had been shown with the synthetic mixtures of hydrocarbons that the filtrate was free of aromatic material until a rise in refractive index was noted. As a comparison it was found that material purified by the silica gel was lower in refractive index by 0.0001 than the raffinate from treatment with a nitrating mixture. Further fractions of filtrate were collected until the refractive index attained that of the oil being filtered, at which time the gel had become saturated. This material was refiltered.

The columns of saturated gel were allowed to drain until oil ceased to flow, after which adhering oil was displaced by the addition of water at the top. The gel was then removed from its tube and the adsorbed oil recovered by shaking with water or distilling with steam.

In table 6 are listed the volumes and refractive indices of the fractions of petroleum distillate before and after filtering them through silica gel. The volumes listed for the fractions of adsorbed material are large in proportion to the aromatic content of the original distillate because some of the oil adhering to the gel was mixed with the fraction adsorbed. This caused a correspondingly lower refractive index for the combined fraction than that for the adsorbed material alone.

This experiment with one petroleum fraction shows that silica gel adsorption should prove to be a useful tool in the investigation of the composition of petroleum distillates.

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EFFECT OF ALKALIES ON WOOL

By Milton Harris [1]

ABSTRACT

Data on the effect of various alkaline reagents on the physical and chemical properties of wool yarn are presented. When wool is treated with dilute sodium-hydroxide solutions, a rapid splitting off of a portion of the sulphur occurs. On continued treatment, the sulphur content of the residual wool approaches a constant value of about 1.8 percent. The results indicate that the alkaline treatment has changed a portion of the sulphur to a form which tends to resist further splitting from the molecule. Oxidizing and reducing agents attack the disulphide groups and make wool more susceptible to alkaline treatments. The susceptibility of untreated wool to alkaline reagents appears to be closely associated with the lability of its sulphur in alkaline solutions.

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I. INTRODUCTION

The effect of alkalies on wool has been studied by many workers, generally from the standpoint of the effect of these reagents on the physical properties of the fiber. Wool fibers deteriorate rapidly in dilute solutions of sodium hydroxide. Buntrock (1),[2] Washburn (2), Matthews (3), and Speakman (4) showed, however, that when the concentration is increased above 15 percent, the strength of wool yarn begins to increase and reaches a maximum with a 38-percent sodium-hydroxide solution, at which point the strength of the yarn is 30 percent greater than the original strength. Speakman further demonstrated that the elastic property of a single fiber is unaffected after immersion in a 38-percent caustic-soda solution, and that the increase in strength of the wool yarn is due to surface gelatinization, which causes fibers to bind together in the dried yarn. Chapin (5) studied

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[2] The figures in parentheses here and elsewhere in the text refer to the numbered references at the end of this paper.

the relative effects of sodium and potassium carbonates and soaps on wool and, for equal molecular concentrations, found them to be about the same.

Recent investigations by Goddard and Michaelis (6), Speakman (7), Pulewka (8), and Marriott (9) have shown that when wool and other keratins are treated with alkaline reducing agents, the disulphide linkages in the molecule are split and the physical structure of the fiber is destroyed. Goddard and Michaelis stated that the reducing agents acted on wool without bringing about any appreciable chemical alteration, other than that concerned with sulphur. Kuster and Koppel (10), however, found that as wool dissolved in sodium-sulphide solutions, a part of it undergoes disintegration with the formation of ammonia and diffusible, nitrogenous, cleavage products.

The present investigation was undertaken to obtain quantitative data on the effect of alkalies on both the physical and chemical properties of wool. Such data are of importance in interpreting the susceptibility of wool to alkaline reagents.

II. MATERIALS AND METHODS

White worsted yarn prepared from raw wool which had been extracted with Stoddard solvent and washed with water, but which had received no previous chemical treatment, was used in this work. The yarn was further purified by extractions with alcohol and ether for 6 hours each and then washed with water at 125° F. All specimens were thoroughly conditioned and tested in a room maintained at a relative humidity of 65 percent and a temperature of 70° F. The conditioned wool contained 14.3 percent of nitrogen, 0.02 percent of ammonia nitrogen, 3.16 percent of sulphur, and 14.4 percent of moisture.

The breaking-strength tests of the yarn were made by the single-strand method on a pendulum-type machine having smooth grips of the drum type, 1 inch in diameter. The distance between the centers of the drums was 10 inches. The values reported are the averages of 25 determinations.

The resiliency tests were made, employing a compressometer (11). The compressional resilience of the specimen is the amount of work recovered from the specimen when the pressure is decreased from 2.0 to 0.1 pound per square inch, expressed as a percentage of the work done on the specimen when the pressure is increased from 0.1 to 2.0 pounds per square inch. The measurements were made on four layers of yarn, wound on metal frames made from thin brass plates, 2¾ by 2¾ by $\frac{1}{10}$ inch, from the center of which a 2-inch square had been cut. Two layers were put on the frames in each direction, each layer containing nine ends per inch.

The total nitrogen was determined by the Kjeldahl method, the ammonia nitrogen by distillation from magnesium oxide suspension, the total sulphur by the oxygen-bomb method (12) and the cystine sulphur by the Sullivan method (13). An ammoniacal sodium-nitroprusside solution was used for the qualitative detection of the sulphydryl group.

The yellowing of the wool by the alkaline treatment was determined by measuring the reflectance of the specimen with respect to a magnesium-oxide standard at wave length 435.8 millimicrons with a Martens photometer, mercury-arc lamp, and suitable filter.

III. RESULTS AND DISCUSSION

1. EFFECT OF ALKALINE REAGENTS ON WOOL YARN

Four-gram samples of wool yarn were treated with 200-ml portions of sodium-carbonate and sodium-hydroxide solutions of various concentrations at a temperature of 125° F for 30 minutes. The supernatant liquor was poured off, the wool washed for 4 hours in running distilled water, and then conditioned in an atmosphere of 65 percent relative humidity and 70° F. The effects of the treatments on the physical and chemical properties of the wool are shown in tables 1 and 2. The results indicate that under the conditions of these experiments, there is no appreciable damage done to wool in sodium-carbonate solutions of concentrations lower than about 4 grams per liter (pH 11.1), and in sodium-hydroxide solutions lower than about 0.038 g per liter (pH 11.8). Above these concentrations, the loss in weight of wool, nitrogen, and sulphur increases and the compressional resilience and the reflectance decrease with increasing alkali concentration. The breaking strength showed no significant changes.

TABLE 1.—*Effect on wool of aqueous sodium-carbonate solutions at 125° F for 30 minutes*

Concentration of Na_2CO_3	pH	Nitrogen in mother liquor	Sulphur content	Reflectance [1] R_X/R_{MgO}	Breaking strength	Compressional resilience
g/liter		*mg/wool*	*Percent*		kg	*Percent*
0	6.80	0.14	3.16	0.481	1.19	52
0.1	10.33	.20	3.17	.480	1.18	51
0.5	10.70	.17	3.16	.480	1.19	53
1.0	10.89	.15	3.15	.481	1.28	52
2.0	11.02	.18	3.17	.482	1.26	50
4.0	11.00	.40	3.12	.482	1.25	50
7.0	11.24	.61	3.11	.469	1.26	48
10.0	11.30	.65	3.03	.469	1.21	43

[1] The values represent the fraction of incident light reflected. The darker (or yellower as in this case) the specimen, the smaller the value for light reflected.

TABLE 2.—*Effect on wool of aqueous sodium-hydroxide solutions at 125° F for 30 minutes*

Concentration NaOH	Original pH	pH of mother liquor	Loss in weight of wool	Nitrogen in mother liquor	Sulphur content of wool after treatment	Reflectance R_X/R_{MgO}	Breaking strength	Compressional resilience
mg/liter			*Percent*	*mg/g wool*	*Percent*		kg	*Percent*
0.0	6.80	6.68	0.61	0.09	3.15	0.475	1.20	51
0.38	9.11	6.90	.60	.10	3.16	.471	1.19	52
3.8	10.83	8.77	.65	.08	3.17	.474	1.12	50
19.2	11.49	10.14	.69	.08	3.15	.476	1.20	52
38.3	11.82	11.33	.67	.11	3.03	.467	1.16	53
153.2	12.41	12.26	1.36	.84	2.93	.460	1.14	49
268.1	12.61	12.49	2.14	1.79	2.74	.463	1.19	48
383.0	12.73	12.66	2.55	2.59	2.55	.455	1.16	35

The effect of various other alkaline reagents was determined by treating 4-gram samples of the wool yarn with 200-ml portions of 0.25-percent solutions of soap, borax, trisodium phosphate, sodium carbonate, and sodium metasilicate, all of which had been brought to pH 12.2 by the addition of sodium hydroxide. The temperature was 150° F and the time of treatment 30 minutes. The skeins were

washed for 4 hours in running distilled water and conditioned. The results are recorded in table 3. The data indicate that at pH 12.2, the solutions of sodium carbonate and trisodium phosphate cause the greatest chemical degradation of the wool. Duplicate experiments with these materials without the addition of sodium hydroxide were not made. The specimens treated with the soap solution were the whitest and most resilient, but showed the greatest decrease in breaking strength. The decrease in strength is attributed to the fact that the soap solution kept the wool yarn soft and fluffy, whereas in the yarn treated with other alkaline solutions, the fibers were matted and stuck together.

TABLE 3.—*Effect on wool of 0.25-percent solutions of various reagents brought to* pH *12.2 with* NaOH

[Time of treatment was 30 minutes and the temperature 150° F]

Reagent	Loss in weight			Reflectance R_X/R_{MgO}	Breaking strength	Compressional resilience
	Wool	Sulphur	Nitrogen			
	mg/g	mg/g	mg/g		kg	*Percent*
Sodium hydroxide	23.0	6.6	3.37	0.424	1.22	44
Soap	19.1	5.9	2.85	.477	.94	51
Borax	20.8	7.6	2.96	.429	1.14	44
Trisodium phosphate	24.8	8.4	3.83	.425	1.12	42
Sodium carbonate	26.0	8.2	3.66	.432	1.10	43
Sodium metasilicate	20.6	6.9	3.06	.442	1.13	44

2. NATURE OF THE ACTION OF ALKALIES ON THE SULPHUR OF WOOL

Although wool contains about five times as much nitrogen as sulphur by weight, the data in table 3 show that about twice as much sulphur as nitrogen was removed from the wool under the conditions of the experiments. This indicated that the susceptibility of wool to alkalies is closely related to the lability of its sulphur in alkaline solutions. It seemed pertinent, therefore, to study the effect of the continued action of alkali on wool, and to determine the rate of removal of sulphur and nitrogen from the wool molecule.

Six-gram samples of wool were treated with 300-ml portions of 0.065 *N* sodium-hydroxide solutions at 150° F for various lengths of time, washed for 4 hours in running distilled water and conditioned. The loss in weight, and the moisture and sulphur contents of the yarns were determined. Aliquots of the mother liquors were analyzed for total and ammonia nitrogen, and sulphur. The results are given in table 4, and are shown graphically in figure 1. The losses in total and ammonia nitrogen are approximately proportional to the loss in weight of wool. The loss of sulphur, however, took place at a more rapid rate until the sulphur content of the wool had dropped to about 1.8 percent, after which the loss was also approximately proportional to the loss in weight of the wool. It is of interest to note that after 4 hours' treatment only 9 percent of the wool had been lost, 41 percent of the sulphur had been lost, and the sulphur content of the treated wool had dropped to 1.86 percent. Similarly after 48 hours' treatment, 66 percent of the wool was lost, but the sulphur content of the residual wool was still 1.87 percent. The broken curve in figure 1 represents the theoretical amount of sulphur that would be lost if the sulphur had split off as an integral part of the wool molecule.

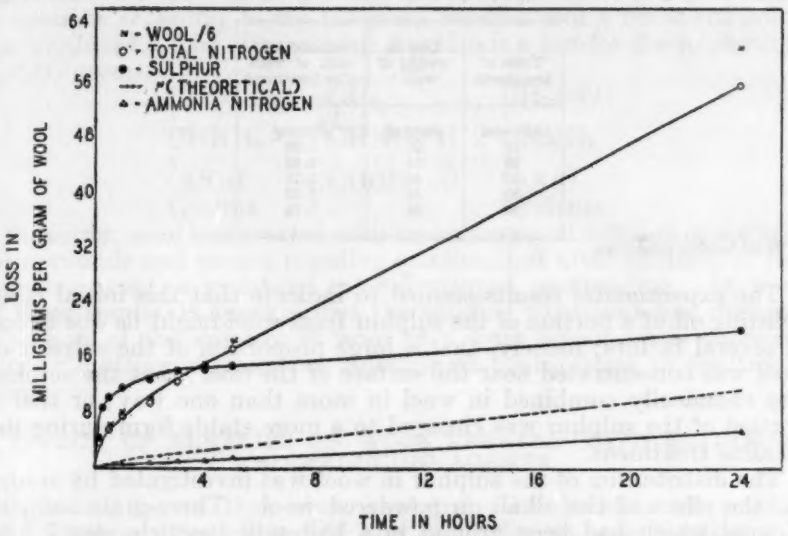


FIGURE 1.—*Effect on wool of the continued action of 0.065* N NaOH *at 150°* F.

TABLE 4.—*Effect on wool of the continued action of 0.065 N sodium-hydroxide solution at 150°* F

Time of treatment	Loss in weight of wool	Total nitrogen in mother liquor	Ammonia nitrogen in mother liquor	Loss in sulphur content of wool		Sulphur content of wool after treatment	Moisture content of conditioned wool after treatment
Minutes	*Percent*	mg/g	mg/g	[b]mg/g	[c]mg/g	*Percent*	*Percent*
10	2.74	3.7	----------	4.4	4.0	2.76	14.4
20	3.42	4.7	----------	8.8	7.4	2.42	14.3
30	3.87	5.5	0.55	10.1	9.7	2.34	14.4
40	4.27	6.0	----------	10.4	9.8	2.21	14.2
50	4.55	6.5	----------	10.9	10.2	2.20	14.4
Hours							
1	4.83	7.5	.79	11.6	11.3	2.18	14.2
2	5.97	9.3	.98	12.8	12.1	1.97	14.4
3	8.38	12.6	1.26	14.0	13.6	1.90	14.5
4	9.11	14.6	1.37	14.5	14.0	1.86	14.3
5	11.20	17.7	1.79	14.9	14.8	1.85	14.4
24	[a]36.00	55.1	5.07	20.0	----------	1.82	15.1
48	[a]66.00	92.8	8.02	25.5	----------	1.87	16.6

[a] The residual wool after 24- and 48-hour treatment was gelatinous and a portion of the fiber was lost during washing. The accuracy of these values is questionable.
[b] Calculated from the sulphur content of the residual wool. The sulphur in the wool was determined by the oxygen-bomb method.
[c] Sulphur found in the mother liquor. It was determined by treating an aliquot with *N* hydrochloric-acid solution saturated with bromine. The solution was allowed to stand on a steam bath for ½ hour and the sulphur determined as barium sulphate. It has been shown that the sulphur in wool or cystine is not oxidized to sulphate under these conditions. This indicates that the sulphur found by this method is split off from the wool.

When specimens of the wool yarn were treated with 0.25 *N* sodium-hydroxide solutions under the conditions described, the sulphur content of the residual wool became constant after about 20 minutes at about 1.8 percent. The results are given in table 5.

TABLE 5.—*Effect on wool yarn of 0.25 N sodium-hydroxide solution at 150° F*

Time of treatment	Loss in weight of wool [1]	Sulphur content of wool after treatment
Minutes	*Percent*	*Percent*
10	22	1.91
20	34	1.85
40	46	1.78
60	58	1.83
90	68	1.79

[1] Wool became gelatinous.

The experimental results seemed to indicate that this initial rapid splitting off of a portion of the sulphur from wool might be due to one of several factors; namely, that a large proportion of the sulphur of wool was concentrated near the surface of the fiber; that the sulphur was chemically combined in wool in more than one way; or that a portion of the sulphur was changed to a more stable form during the alkaline treatment.

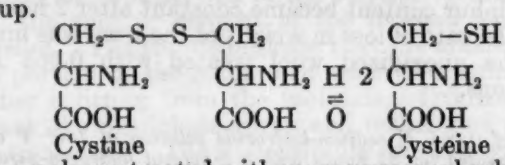
The distribution of the sulphur in wool was investigated by studying the effect of the alkali on powdered wool. Three-gram samples of wool which had been ground in a ball mill (particle size 0.3 to 2μ) were put in 150-ml portions of 0.065 *N* sodium-hydroxide solutions at 150° F for various lengths of time, after which the alkaline solutions were quickly cooled in ice water, centrifuged for 5 minutes at 2,200 rpm and the supernatant liquid decanted. Distilled water was mixed with the residue and the resulting suspension again centrifuged. This rinsing was repeated six times. The powder was dried for 24 hours at 105 to 110° C and the total sulphur determined. The results in table 6 show that the sulphur content decreased at a slightly faster rate than that of the wool yarn, but became constant after 3 hours at about 1.8 percent (calculated on basis of 14.4 percent of moisture). The close agreement of the results obtained on the wool yarn and wool powder indicates that the sulphur is uniformly distributed throughout the wool fiber.

TABLE 6.—*Effect on powdered wool of 0.065 N sodium-hydroxide solution at 150° F*

Time of treatment	Sulphur content of wool after treatment	Time of treatment	Sulphur content of wool after treatment
Hours	*Percent*	*Hours*	*Percent*
1	2.00	4	1.80
2	1.95	5	1.78
3	1.85	24	1.81

That the bulk of the sulphur in wool is not combined in more than one way and is practically entirely present as cystine sulphur, has been shown by Rimington (14) and by Sullivan and Hess (13). Employing the Sullivan method for the determination of cystine, it was found that at least 96 percent of the sulphur of the wool used in these experiments was cystine sulphur. The presence of practically all of the sulphur in one form was further demonstrated qualitatively by the following procedure. When cystine was treated with an ammoniacal solution of sodium nitroprusside no reaction occurred.

On addition of potassium-cyanide solution, the cystine was reduced to cysteine according to the following reaction and a violet-red color was produced. The nitroprusside reaction is a test for the sulphydryl (—SH) group.



Cystine Cysteine

Similarly, wool was treated with an ammoniacal solution of sodium nitroprusside and gave a negative reaction, but after addition of the reducing agent, a violet-red color developed on standing. In view of these results, it appears that the alkaline treatment has changed a portion of the sulphur of wool to a form which tends to resist further splitting off from the molecule on continuation of the treatment.

3. EFFECT OF ALKALIES ON WOOL TREATED WITH OXIDIZING AND REDUCING AGENTS

It is well known that when wool and other keratins are treated with alkaline reducing agents, the disulphide linkage (cystine sulphur) is split. Oxidizing agents also react with the disulphide groups in keratins, but their action is not specific for these groups, since they are known to attack other parts of the protein molecule. The oxidation of the disulphide group proceeds very slowly and it is only with difficulty that these linkages are split by oxidation methods.

It is obvious that a number of oxidation products of cysteine and cystine are possible. The intermediate oxidation products have never been definitely isolated although Lavine and Toennies (15), in studies of the oxidation of cystine in nonaqueous media, obtained a precipitate with a composition approximating that of a sulphoxide. There is, as will be shown later, some evidence which indicates the formation of these intermediate products during the oxidation of wool.

The effect of alkali on oxidized wool was studied. Wool yarn was treated with 3-percent hydrogen-peroxide solution for 24 hours at room temperature, after which the yarn was thoroughly rinsed and conditioned. The sulphur content of the treated wool was slightly lower (3.12 percent), but the physical properties were the same as those of the untreated wool. When the oxidized wool was treated with an alkaline nitroprusside solution, a negative test was obtained, but on addition of sodium-cyanide solution, a violet-red color was produced. The color obtained with the nitroprusside test developed much more rapidly with the oxidized wool than with the unoxidized wool. However, when equal amounts of the treated and untreated wool were dissolved in normal sodium-hydroxide solutions and equal amounts of sodium nitroprusside were added to each, the solution of the unoxidized wool was the more deeply colored. The results show that oxidation has made the disulphide group more labile to alkaline reagents, but has also reduced the number of potential sulphydryl groups in the oxidized wool. This suggests the possibility that under the conditions of the oxidation in these experiments, intermediate products such as the following are formed:

$$R\text{–}SO\text{–}S\text{–}R \text{ or } R\text{–}SO_2\text{–}S\text{–}R$$

Samples of the oxidized wool were treated with 0.065 *N* sodium-hydroxide solution as previously described. The loss in weight of the wool and the sulphur content of the wool after treatment are given in table 7. The sulphur content became constant after 2 hours at about 1.96 percent. The rate of loss in weight of the wool was much greater than that of the unoxidized wool treated with 0.065 *N* sodium-hydroxide solutions.

TABLE 7.—*Effect of 0.065 N sodium-hydroxide solution at 150° F on wool yarn which had been treated for 24 hours with a 3-percent hydrogen-peroxide solution*

Time	Loss in weight of wool	Sulphur content of wool after treatment
Hours	*Percent*	*Percent*
½	7.8	2.41
1	9.9	2.30
2	12.1	2.02
3	14.3	1.97
5	18.9	1.95
24	48.8	1.96

When samples of the wool yarn were treated with 0.065 *N* sodium hydroxide solutions containing 1 percent of sodium sulphide, and with 1 percent sodium-sulphide solutions alone, the wool fibers deteriorated rapidly. All of the samples became gelatinous within a few minutes, which prevented an accurate determination of the loss in weight of the wool. It was estimated that for the shortest period of time (½ hour), the wool lost more than 50 percent in weight. The sulphur contents of the residual wool are given in table 8. Addition of the reducing agent splits the disulphide linkage and the wool rapidly loses its fibrous structure.

TABLE 8.—*Sulphur contents of wool treated with* 0.065 *N sodium-hydroxide solution containing 1 percent of sodium sulphide and with a 1-percent sodium-sulphide solution alone at 150° F*

Time	Sulphur content of wool treated with 0.065 *N* NaOH+1% of Na_2S	Sulphur content of wool treated with 1% of Na_2S
Hours	*Percent*	*Percent*
½	3.03	3.04
1	2.94	
2	2.86	2.77

It is of interest to note that while the wool deteriorates very rapidly in the presence of alkaline-reducing agents, the sulphur content of the residual wool was much higher than when sodium hydroxide alone was used. This suggests that the disulphide sulphur is more labile to alkaline treatment than the sulphydryl sulphur. This is in agreement with the results of Gortner and Thor (16), who found that cysteine is more stable toward alkalies than cystine.

IV. CONCLUSIONS

When wool is treated with dilute sodium-hydroxide solutions, a rapid splitting off of a portion of the sulphur occurs. On continued treatment, the sulphur content of the residual wool approaches a constant value. The results indicate that the alkaline treatment has changed a portion of the sulphur of wool to a form which tends to resist further splitting from the molecule. Oxidizing and reducing agents attack the disulphide group and make wool more susceptible to alkaline treatment. The susceptibility of wool to alkaline reagents appears to be closely associated with the lability of its sulphur in alkaline solution.

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RESEARCH PAPER RP811

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INFLUENCE OF SULPHONATED COD-LIVER OIL ON THE DETERIORATION OF VEGETABLE-TANNED LEATHERS BY SULPHURIC ACID

By Everett L. Wallace, Charles L. Critchfield, and John Beek, Jr.

ABSTRACT

The deterioration by sulphuric acid of leather containing 10 percent of sulphonated cod-liver oil was compared with that of leather containing no sulphonated oil. It was found that the addition of oil did not protect the leather from the effect of the acid. The addition of oil apparently increased the effect of the acid on the leather tanned with chestnut-wood extract. All of the leather which had a pH less than 3.0 showed deterioration after 2 years' aging.

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I. INTRODUCTION

An extended study of the effect of sulphuric acid on leather has been in progress at the National Bureau of Standards for about 8 years. The object has been to determine the influence of various factors on the deterioration of leather by acid. It was shown [1] that the addition of 20 percent of a mixture of equal parts of beef tallow and cod-liver oil has no significant effect on the deterioration of leather by sulphuric acid. The present phase of the investigation was undertaken in order to determine the influence of the addition of sulphonated cod-liver oil on the effect of sulphuric acid on leather.

II. MATERIALS AND METHODS USED

Two lots of five hides each were used to prepare the leather. The tanning process was carried out in the experimental tannery at this Bureau, one lot being tanned with chestnut-wood extract, the other with quebracho-wood extract. The results of the analysis of the leathers before treatment are given in table 1. The official methods of the American Leather Chemists Association were used for the analyses, except for the total sulphur, which was determined by a nitric-acid-bromine-oxidation method.[2]

[1] J. Am. Leather Chem. Assn. 26, 667 (1931).
[2] J. Am. Leather Chem. Assn. 26, 444 (1931).

TABLE 1.—*The chemical analyses of leathers before treatment*

[The results are expressed as percentage of the leather, excepted for degree of tannage and pH]

Tanning material	Chestnut	Quebracho
Water-soluble	7.67	9.00
Hide substance	50.15	47.93
Grease (petroleum-ether extract)	4.18	3.14
Moisture	10.66	9.93
Insoluble ash	0.10	0.10
Combined tannin [1]	27.24	29.90
Total	100.00	100.00
Degree of tannage [2]	54	62
Soluble tannins	6.31	7.68
Soluble nontannins	1.36	1.32
Total ash	0.26	0.16
Total sulphur (as H_2SO_4)	0.14	0.10
pH [3] (glass electrode)	4.18	5.45

[1] Determined by difference.
[2] The ratio of combined tannin to hide substance.
[3] 4.9 g of dry leather in 100 ml of distilled water.

The sulphonated cod-liver oil was a commercial product, containing 2.08 percent of sulphur, calculated as sulphuric acid, 2.3 percent of ash, and 8.2 percent of water. The oil was ammonia neutralized.

The distribution of the leather relative to hide location, for the treatment with acid and oil, was like that previously described,[3] except that each value of deterioration reported is calculated from the average of 30 samples instead of 42. The amounts of acid added were approximately 0, 1, 2, and 3 percent. After the acid treatment, one-half of the leather was oiled with sulphonated cod-liver oil. Each test block was weighed and the oil at 40° C was rubbed into the leather until the gain in weight indicated an oil content of 10 percent. The results of the total sulphur and pH determinations on the treated leather are given in table 2.

The leather was aged at a temperature of 70° F and a relative humidity of 65 percent. Samples for the determination of tensile strength were taken 0, 6, 12, 18, and 24 months after treatment.

III. RESULTS

The quantity used as a criterion of deterioration is the ratio of the average tensile strength of a group of aged samples to the average tensile strength of the corresponding group before treatment. Table 2 shows these ratios for the five aging periods. The results for the 24 months' aging period are shown in graph A, figure 1, plotted against the pH of the leather before aging.

[3] J. Research NBS 14, 121 (1935) RP761 and J. Am. Leather Chem. Assn. 30, 91 (1935).

TABLE 2.—*The analysis of the treated leather and the results of the determinations of the relative tensile strength*

Oil added	Acid added	pH	Percentage tensile strength retained after treatment and aging				
			Age (months)—				
			0	6	12	18	24
CHESTNUT							
0	0.00	4.18	100	96	93	98	92
0	1.17	3.05	97	95	96	98	93
0	2.18	2.72	94	90	86	83	80
0	3.16	2.39	91	81	73	70	61
10	0.00	4.32	108	100	103	108	104
10	0.83	3.17	104	99	101	104	96
10	1.85	2.76	102	96	93	91	85
10	2.95	2.46	92	77	71	68	66
QUEBRACHO							
0	0.00	5.45	98	97	95	100	99
0	0.88	3.55	99	98	99	104	98
0	1.54	2.98	101	99	97	101	97
0	2.42	2.54	96	96	92	93	90
10	0.00	5.58	107	103	105	108	109
10	0.85	3.68	101	100	100	106	108
10	1.43	3.07	108	106	105	108	107
10	2.20	2.53	103	98	99	97	93

As the addition of oil increased the tensile strength of the leather, a direct comparison of the leathers, with and without oil, shows not only the influence of the oil on the deterioration of the leather by acid, but also the effect of the oil on the leather. In order to make a proper comparison of the leathers, the relative tensile strengths given in table 2 were reduced to a common basis by subtracting the values for the leather containing no added acid from the other values in the same group with respect to oil treatment and aging period. Taking the chestnut leather without added oil for example, the figure 92 was subtracted from each of the values given for the 24 months' period. The resulting corrected values show the effect of the acid on the tensile strength of the leather. The results for the 24 months' aging period are shown in graph B, figure 1, plotted against the pH of the leather.

There is apparently a difference between the two kinds of leather with respect to the effect of the oil on their deterioration by acid. Graph A, figure 1, shows that the chestnut leather containing acid was not improved with respect to its deterioration by acid by the addition of oil except as a result of the increase of the pH. That is, after 24 months' aging, the leather containing added oil was no better than that to which no oil was added. In contrast to this, the quebracho leather containing added oil and acid was considerably stronger after 24 months' aging than that containing no added oil. This difference is shown also in graph B, where the effect of the acid on the chestnut leather containing oil appears to be greater than on the other leather. Although the appearance of this effect may be a result of experimental error, it does not seem probable that this is the case, as a direct comparison of the tensile strengths of the oiled and unoiled chestnut leather gives the same indication for the 12, 18, and 24 months' aging

periods. However, it is certain that the oil did not decrease the effect of the acid on either the chestnut or quebracho leather.

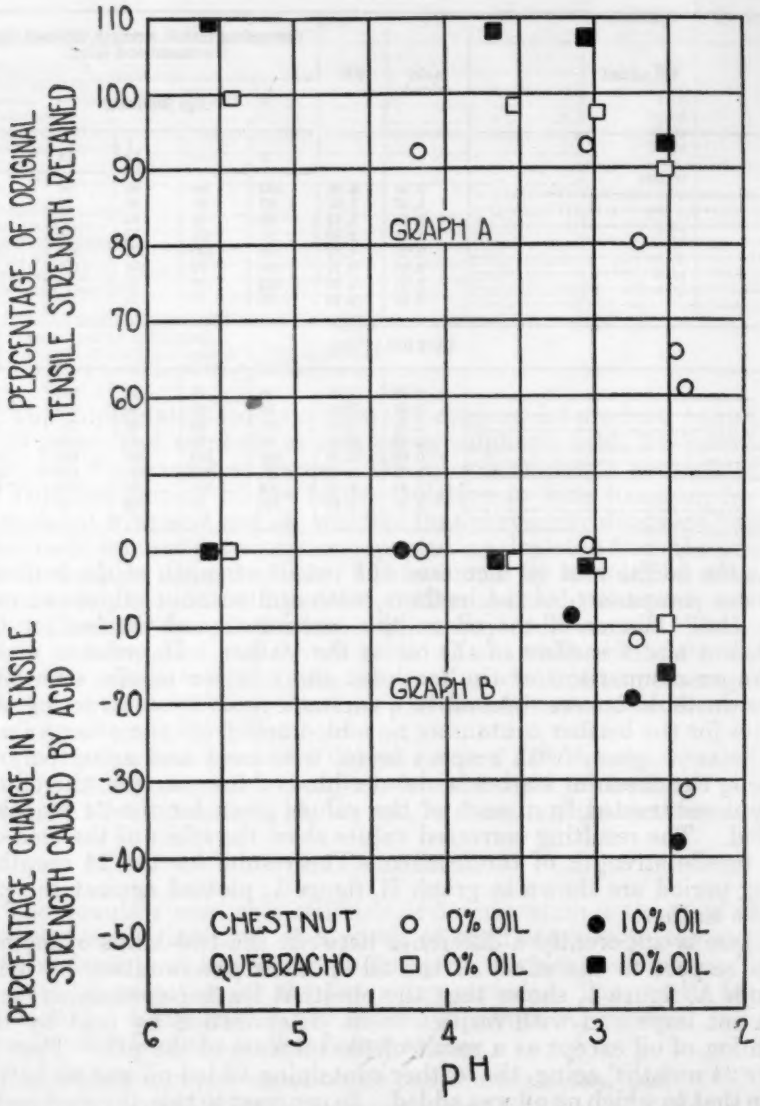

FIGURE 1.—*Results of the 24 months' aging tests plotted against the* pH *of the leather before aging*

It should be noticed that in no case did a sample with a pH lower than 3.0 before aging retain its original tensile strength, after aging 2 years. This is in accordance with previous findings in this study.[4]

[4] J. Research NBS 14 (1935) RP761. J. Am. Leather Chem. Assn. 30, 91 (1935).

IV. SUMMARY

The influence of the addition of 10 percent of sulphonated cod-liver oil on the deterioration by sulphuric acid of leathers tanned with chestnut- and quebracho-wood extracts was determined by comparing the change with age of the tensile strength of leather with and without added oil.

The addition of the oil apparently increased the effect of the acid on the chestnut leather. It had no influence on the effect of acid on the quebracho leather, except for the sample containing the most acid. The tensile strength of the leather containing no acid was increased by the addition of oil.

Leather having a pH lower than 3.0 before aging showed deterioration after 2 years' aging.

WASHINGTON, May 15, 1935.

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INFRARED ARC SPECTRUM OF CHROMIUM

By C. C. Kiess

ABSTRACT

The new types of plates, sensitive to infrared light, have made it possible to photograph the arc spectrum of chromium out to 11610 A. Approximately 200 wave lengths have been recorded for this region. Most of these are classified as combinations between terms already known and the new terms, mostly of the triplet system, which are given in the paper.

I. INTRODUCTION

Fifteen years ago a survey of the arc spectrum of chromium, extending from 5500 A to the infrared limit photographically attainable at that time, was made in the spectroscopic laboratory of the National Bureau of Standards.[1] This work not only bridged the gap that had previously existed between the longest known wave length in the red and the beginning of Randall and Barker's[2] list of infrared lines, observed radiometrically, but also pointed out the first regularities to be noted for this spectrum. An outstanding feature of the chromium arc spectrum is the presence of several intense triplets of which some lie in proximity to the boundaries between the traditional actinic, visible, and infrared regions. Thus, for example, the infrared chromium spectrum may be considered as that portion composed of wave lengths greater than those of the strong triplet at 7356, 7400, and 7462 A. The production of new types of photographic plates in recent years by the Eastman Kodak Co., far surpassing in sensitivity those used in this earlier work, has made it desirable to resurvey the infrared region of the chromium arc spectrum, especially since our present knowledge of its term structure enables us to predict lines not observed in the earlier work. It is the purpose of this paper to describe the infrared arc spectrum of chromium as revealed by this more recent investigation.

II. RESULTS

The observations were made with the concave-grating spectrographs of the National Bureau of Standards, according to our usual practice, which has been described frequently in earlier papers.[3] The grating ruled with 20,000 lines per inch, giving a dispersion of 3.5 A/mm in the first order, was used in making the spectrograms out

[1] Kiess and Meggers, BS Sci. Pap. **16**, 58 (1920) S372.
[2] Astrophys. J. **49**, 42 (1919).
[3] BS J. Research **9**, 309 (1932) RP473.

to 9100 A. Beyond that limit all the spectrograms were made with the 7,500-lines-per-inch grating, dispersion 10.3 A/mm. In all the exposures, which varied from a few minutes to two hours, the light source was an arc between lumps of very pure chromium metal between which a direct current of 6 or 7 amperes was maintained under a potential of 220 volts. For each region photographed the appropriate sensitive plate, as recommended by Mees,[4] was employed after it had been hypersensitized in an ammonia bath.[5]

TABLE 1.—*Infrared wave lengths of* Cr I

λ_{air}	Intensity	Wave number (vac.)	Term combination	λ_{air}	Intensity	Wave number (vac.)	Term combination
11610.48	15	8610.55	$z^5P_3^\circ$—c^5D_4	9934.52	2	10063.16	$y^7P_3^\circ$—c^5S_2
11484.50	15	8705.01	$z^5P_2^\circ$—c^5D_3	9904.47	8	10093.69	a^3D_3—$z^3D_3^\circ$
11472.93	10	8713.79	$z^5P_3^\circ$—c^5D_3	9900.87	15	10097.36	a^3P_2—$z^3P_2^\circ$
11397.96	12	8771.10	$z^5P_1^\circ$—c^5D_2	9845.19	1	10154.46	$y^7P_3^\circ$—c^5S_2
11390.63	15	8776.74	$z^5P_2^\circ$—c^5D_2	9773.30	10	10229.15	a^3D_2—$z^3D_3^\circ$
11379.26	5	8785.52	$z^5P_3^\circ$—c^5D_2	9758.71	2	10244.45	
11339.16	15	8816.58	$z^5P_1^\circ$—c^5D_1	9752.84	4	10250.62	a^3P_1—$z^3P_0^\circ$
11331.88	10	8822.25	$z^5P_2^\circ$—c^5D_1	9734.52	50	10269.91	a^5G_2—$z^5F_1^\circ$
11310.69	12	8838.78	$z^5P_1^\circ$—c^5D_0	9730.32	25	10274.34	a^3D_3—$z^3D_3^\circ$
11157.03	25	8960.51	$y^7P_4^\circ$—e^7S_3	9670.48	50	10337.91	a^5G_3—$z^5F_2^\circ$
11044.64	5	9051.69	b^5D_1—$z^5D_0^\circ$	9667.20	25	10341.42	a^5G_2—$z^5F_2^\circ$
11015.63	30	9075.53	$y^7P_3^\circ$—e^7S_3	9626.30	4	10385.36	a^3P_1—$z^3P_1^\circ$
10957.19	12	9123.93	b^5D_2—$z^5D_1^\circ$	9574.25	50	10441.82	a^5G_4—$z^5F_3^\circ$
10929.90	10	9146.71	b^5D_0—$z^5D_1^\circ$	9571.76	25	10444.54	a^5G_3—$z^5F_3^\circ$
10905.83	25	9166.90	$y^7P_2^\circ$—e^7S_3	9568.58	4	10448.01	a^5G_2—$z^5F_3^\circ$
10902.90	2	9169.37		9520.13	4	10501.18	
10821.62	12	9238.23	b^5D_3—$z^5D_3^\circ$	9447.00	50	10582.47	a^5G_5—$z^5F_4^\circ$ a^5G_4—$z^5F_4^\circ$
10816.91	8	9242.26	b^5D_2—$z^5D_2^\circ$	9444.36	5	10585.43	a^5G_3—$z^5F_4^\circ$
10801.37	12	9255.55	b^5D_1—$z^5D_2^\circ$	9409.78	3	10624.45	
10672.17	18	9367.60	b^5D_3—$z^5D_3^\circ$	9398.13	1	10637.50	
10667.53	15	9371.68	b^5D_2—$z^5D_3^\circ$	9362.06	10	10678.48	a^3P_1—$z^3P_2^\circ$
10647.66	12	9389.17	b^5D_4—$z^5D_3^\circ$	9313.55	8	10734.10	a^3P_0—$z^3P_1^\circ$
10631.42	2	9403.50	$u^5F_5^\circ$—e^5G_6	9294.17	20	10756.48	a^5G_5—$z^5F_5^\circ$ a^5G_4—$z^5F_5^\circ$
10550.12	3	9475.97	b^5D_1—$z^3P_2^\circ$	9290.44	50	10760.80	a^5G_6—$z^5F_5^\circ$
10509.96	10	9512.18	b^5D_2—$z^5D_2^\circ$	9263.97	20	10791.55	a^3F_2—$z^3G_3^\circ$
10486.24	20	9533.70	b^5D_4—$z^5D_4^\circ$	9208.29	25	10856.80	a^3F_4—z^3G_4
10416.75	2	9597.30	b^5D_2—$z^3P_1^\circ$	9148.45	6	10927.82	a^3F_3—z^3G_4
10217.06	1	9784.87	c^5D_3—x^5F_4	9142.60	8	10934.81	$x^5G_5^\circ$—e^5G_5
10197.05	3	9804.07	a^3P_2—$z^3P_1^\circ$	9141.12	7	10936.58	$x^5G_6^\circ$—e^5G_5
10111.90	1	9886.63	b^5D_3—$z^3P_2^\circ$	9140.51	8	10937.31	$x^5G_4^\circ$—e^5G_4
10089.61	2	9908.48	c^5D_4—$x^5F_5^\circ$	9128.10	2	10952.18	
10083.17	5	9914.80	a^3D_2—$z^3D_1^\circ$	9113.08	2	10970.23	c^5D_4—$x'^5D_3^\circ$
10080.32	15	9917.60	a^3D_1—$z^3D_1^\circ$	9093.76	2	10993.54	
9949.06	20	10048.45	a^3D_2—$z^3D_2^\circ$	9068.30	2	11024.40	c^5D_4—$x'^5D_4^\circ$
9946.30	7	10051.24	a^3D_1—$z^3D_2^\circ$	9059.74	5	11034.82	a^3F_4—$z^3G_5^\circ$

[4] J. Opt. Soc. Am., **25**, 80 (1935).
[5] Burka, J. Franklin Inst., **189**, 25 (1920).

TABLE 1.—*Infrared wave lengths of* Cr I—Continued

λ_{air}	Intensity	Wave number (vac.)	Term combination
9035.86	20	11063.99	$a^3G_3 - z^3G^\circ_3$
9021.69	50	11081.36	$z^5P^\circ_1 - e^5S_2$
9017.10	75	11087.00	$z^5P^\circ_2 - e^5S_2$
9009.95	100	11095.80	$z^5P^\circ_3 - e^5S_2$
8989.19	3	11121.42	
8976.88	25	11136.67	$a^3G_4 - z^3G^\circ_4$
8957.97	2	11160.18	$a^5F_2 - z^5G^\circ_2$
8955.74	6	11162.97	$a^5F_1 - z^5G^\circ_2$
8949.57	3	11170.66	
8947.20	35	11173.62	$a^3G_5 - z^3G^\circ_5$
8943.71	2	11177.99	
8939.20	8	11183.62	$a^5F_2 - z^5G^\circ_3$
8936.48	3	11187.02	$a^5F_4 - z^5G^\circ_4$
8929.45	2	11195.82	$a^5F_5 - z^5G^\circ_5$
8925.75	10	11200.48	$a^5F_3 - z^5G^\circ_4$ $a^3G_3 - z^3G^\circ_4$
8917.14	8	11211.28	$a^5F_4 - z^5G^\circ_5$
8916.20	15	11212.46	$a^5F_5 - z^5G^\circ_6$
8898.60	1	11234.64	
8870.35	2	11270.42	$a^5F_4 - x^5D_3$
8835.67	10	11314.66	$a^3G_4 - z^3G^\circ_3$
8808.84	2	11349.12	$c^5D_1 - u^5P^\circ_2$
8796.16	2	11365.48	
8789.54	1	11374.04	$b^3P_2 - z^3D^\circ_1$
8788.31	1	11375.63	
8786.96	4	11377.37	$c^5D_3 - u^5P^\circ_3$
8784.15	2	11381.02	$c^5D_0 - u^5P^\circ_1$
8773.56	5	11394.75	$c^5D_2 - u^5P^\circ_2$
8767.12	4	11403.12	$c^5D_1 - u^5P^\circ_1$
8753.50	5	11420.87	$b^3P_1 - z^3D^\circ_1$
8743.55	2	11433.86	$b^3P_0 - z^3D^\circ_1$
8732.17	3	11448.77	$c^5D_2 - u^5P^\circ_1$
8718.70	8	11466.45	$c^5D_3 - u^5P^\circ_2$
8716.09	1	11469.89	
8707.95	12	11480.61	$a^5P_1 - z^5D^\circ_0$
8707.42	7	11481.31	$c^5D_4 - u^5P^\circ_3$
8687.47	7	11507.68	$b^3P_2 - z^3D^\circ_2$
8681.89	3	11515.07	$a^5F_3 - x^5D^\circ_4$
8676.00	1	11522.89	
8653.57	1	11552.76	
8652.24	3	11554.53	$b^3P_1 - z^3D^\circ_2$
8643.03	12	11566.84	$a^5P_1 - z^5D^\circ_1$
8636.26	10	11575.91	$a^5P_2 - z^5D^\circ_1$
8609.26	2	11612.21	
8583.01	10	11647.73	$z^5H^\circ_7 - e^5G_6$
8562.56	5	11675.55	$z^5H^\circ_6 - e^5G_5$
8555.54	5	11685.13	$a^5P_1 - z^5D^\circ_2$
8583.20	2	11688.32	$b^3P_2 - z^3D^\circ_3$
8548.83	12	11694.30	$a^5P_2 - z^5D^\circ_2$
8543.72	10	11701.29	$a^5P_3 - z^5D^\circ_2$
8537.80	8	11709.41	$z^5H^\circ_5 - e^5G_4$
8530.40	1	11719.56	$z^5H^\circ_5 - e^5G_5$
8511.02	7	11746.25	$z^5H^\circ_4 - e^5G_3$
8483.36	4	11784.55	$z^5H^\circ_3 - e^5G_2$
8458.11	3	11819.73	
8455.24	12	11823.74	$a^5P_2 - z^5D^\circ_3$
8450.26	15	11830.71	$a^5P_3 - z^5D^\circ_3$
8442.95	2	11841.09	
8418.34	2	11875.57	
8416.58	2	11878.05	
8397.04	6	11905.69	$a^5P_1 - z^3P^\circ_0$
8378.52	10	11932.01	$z^3F^\circ_4 - e^3G_5$
8348.28	20	11975.23	$a^5P_3 - z^5D^\circ_4$
8338.83	5	11988.80	$c^5D_0 - v^5F^\circ_1$
8336.81	8	11991.70	$z^3F^\circ_3 - e^3G_4$
8323.44	5	12010.96	$c^5D_1 - v^5F^\circ_1$
8322.99	3	12011.62	$a^3H_6 - z^3G^\circ_5$
8322.06	20	12012.96	$c^5D_1 - v^5F^\circ_2$
8318.25	8	12018.46	$z^3F^\circ_3 - e^3G_3$
8303.19	6	12040.26	$a^5P_1 - z^3P^\circ_1$
8297.58	3	12048.40	
8296.90	4	12049.39	$a^5P_2 - z^3P^\circ_1$
8290.62	10	12058.52	$c^5D_2 - v^5F^\circ_2$
8287.38	25	12063.23	$c^5D_2 - v^5F^\circ_3$
8286.33	2	12064.76	
8285.72	2	12065.64	
8273.80	3	12083.03	$x^5F^\circ_5 - e^5G_6$
8273.20	3	12083.90	
8264.27	2	12096.96	$x^5F^\circ_4 - e^5G_5$
8261.95	8	12100.36	$a^3H_4 - z^3G^\circ_4$
8240.67	2	12131.61	$c^5D_0 - w^5D^\circ_1$
8238.29	12	12135.11	$c^5D_3 - v^5F^\circ_3$
8235.89	30	12138.65	$c^5D_3 - v^5F^\circ_4$
8225.67	3	12153.73	$c^5D_1 - w^5D^\circ_1$
8224.09	8	12156.06	$a^3H_5 - z^3G^\circ_4$
8218.07	3	12164.97	
8216.28	5	12167.62	$c^5D_1 - w^5D^\circ_2$
8194.87	4	12199.40	$c^5D_2 - w^5D^\circ_1$
8188.77	3	12208.50	
8185.69	5	12213.09	$c^5D_2 - w^5D^\circ_2$
8169.80	5	12236.84	$c^5D_0 - u^5F^\circ_1$
8167.94	4	12239.63	
8166.66	7	12241.55	$c^5D_4 - v^5F^\circ_4$ $c^5D_2 - w^5D^\circ_3$
8163.22	35	12246.70	$c^5D_4 - v^5F^\circ_5$
8155.00	6	12259.05	$c^5D_1 - u^5F^\circ_1$
8128.28	8	12299.35	$c^5D_1 - u^5F^\circ_2$
8124.83	2	12304.57	$c^5D_2 - u^5F^\circ_1$
8119.13	3	12313.21	$c^5D_3 - w^5D_3$
8098.24	5	12344.97	$c^5D_2 - u^5F^\circ_2$
8084.98	10	12365.22	$c^5D_3 - w^5D_4$
8061.27	10	12401.59	$c^5D_2 - u^5F^\circ_3$

TABLE 1.—*Infrared wave lengths of* Cr I—Continued

λ_{air}	Intensity	Wave number (vac.)	Term combination	λ_{air}	Intensity	Wave number (vac.)	Term combination
8050.68	2	12417.92		7910.50	10	12637.95	$z^5H_3^1-e^5G_4$
8045.33	7	12426.16		7908.30	12	12641.47	$z^5H_3^1-e^5G_5$
8018.04	3	12468.45	$c^5D_4-w^5D_4^1$	7885.00	4	12678.82	$c^5D_2-u'\ ^5F_3^1$
8014.88	5	12473.36	$c^5D_3-u^5F_3^1$	7771.74	8	12863.59	
7990.50	10	12511.42		7763.00	4	12878.08	
7989.36	12	12513.21	$c^5D_3-u^5F_4^1$	7749.25	1	12900.93	
7971.31	4	12541.54	$c^5D_3-u'\ ^5F_4^1$	7734.00	3	12926.37	$b^3F_2-z^3F_3^1$
7942.02	20	12587.80	$c^5D_4-u^5F_5^1$	7726.02	3	12939.72	$b^3F_3-z^3F_3^1$
7924.06	3	12616.33	$c^5D_4-u^5F_4^1$	7724.50	1	12942.27	
7917.85	10	12626.23	$z^3H_4^1-e^3G_3$	7722.89	5	12944.96	$b^3F_4-z^3F_4^1$

The new wave lengths, entered in table 1, are the means of from 2 to 12 observations, including those given in the earlier paper. These are referred to the iron standards,[6] which were observed in the second- and third-order spectra in juxtaposition with the first-order chromium spectrum. Following each recorded wave length is an estimated intensity, the wave number in vacuum, and the classification of the line.

The term combinations assigned to the classified lines are based on previously known terms of Cr I and on the new and hitherto unpublished terms given in tables 2 and 3. The term structure of Cr I is built up, theoretically, of septet, quintet, triplet, and singlet systems. Of these, the septets and quintets account for nearly all the prominent lines of the spectrum, which according to King [7] are excited at the lowest temperature stages of his vacuum furnace. Except for three odd terms of the triplet system, all the previously known terms of Cr I belong to the septet and quintet systems. They are given in an earlier paper of this Journal [8] and also by Catalan and Sancho,[9] who, in addition, give a list of classified lines derived from them. The new terms of tables 2 and 3 belong mostly to the triplet system.

TABLE 2.—*Even terms of* Cr I

Term	ν	$\Delta\nu$	Term	ν	$\Delta\nu$
c^5D_4	35397.7	−103.3	a^5F_5	31393.1	15.3
c^5D_3	35501.0	−71.8	a^5F_4	31377.8	13.7
c^5D_2	35572.8	−45.6	a^5F_3	31364.1	9.1
c^5D_1	35618.4	−22.2	a^5F_2	31355.0	2.7
c^5D_0	35640.6		a^5F_1	31352.3	
f^5D_4	55209.0	222.0	e^5G_6	57388.9	6.2
f^5D_3	54987.0	168.3	e^5G_5	57382.7	10.1
f^5D_2	54818.7	146.9	e^5G_4	57372.6	11.4
f^5D_1	54671.8		e^5G_3	57361.2	10.6
f^5D_0			e^5G_2	57350.6	

[6] Trans. Int. Astron. Union, **3**, 77 (1928).
[7] Astrophys. J. **41**, 86 (1915).
[8] Kiess, BS J. Research **5**, 775 (1930) RP229. Note.—The term listed in this paper as $y^5D_3^1$=41124.7 should read 41224.7.
[9] Anales Soc. Espan. Fis. Quim., **19**, 327 (1931).

TABLE 2.—*Even terms of* Cr I—Continued

Term	ν	$\Delta\nu$	Term	ν	$\Delta\nu$
a^3P_2	24093.2		a^3G_5	25038.3	
		581.3			141.0
a^3P_1	23511.9		a^3G_4	24897.3	
		348.7			63.6
a^3P_0	23163.2		a^3G_3	24833.7	
b^3P_2	27223.0		b^3G_5	27816.7	
		47.0			113.1
b^3P_1	27176.0		b^3G_4	27703.6	
		12.9			106.4
b^3P_0	27163.1		b^3G_3	27597.2	
a^3D_3	28637.0		e^3G_5	57990.1	
		−45.2			−1.9
a^3D_2	28682.2		e^3G_4	57992.0	
		2.6			7.1
a^3D_1	28679.6		e^3G_3	57984.9	
b^3D_3	31009.0		a^3H_6	24200.1	
		−19.4			144.2
b^3D_2	31028.4		a^3H_5	24055.9	
		−20.4			122.2
b^3D_1	31048.8		a^3H_4	23933.7	
a^3F_4	25177.2		a^3I_7	31047.8	
		71.1			−1.3
a^3F_3	25106.1		a^3I_6	31049.1	
		165.6			−6.1
a^3F_2	24940.5		a^3I_5	31055.2	
b^3F_4	33113.2				
		52.5			
b^3F_3	33060.7				
		20.5			
b^3F_2	33040.2				

TABLE 3.—*Odd terms of* Cr I

Term	ν	$\Delta\nu$	Term	ν	$\Delta\nu$
$x^3S_1^\circ$	47088.4		$z^3F_4^\circ$	46058.2	
					57.8
			$z^3F_3^\circ$	46000.4	
$y^3S_1^\circ$	49477.0				33.9
			$z^3F_2^\circ$	45966.5	
$z^3P_2^\circ$	34190.7		$y^3F_4^\circ$	49620.6	
		293.4			−29.6
$z^3P_1^\circ$	33897.3		$y^3F_3^\circ$	49650.2	
		134.7			−2.6
$z^3P_0^\circ$	33762.6		$y^3F_2^\circ$	49652.8	
$y^3P_2^\circ$	45734.3		$x^3F_4^\circ$	55207.3	
		15.1			105.5
$y^3P_1^\circ$	45719.2		$x^3F_3^\circ$	55101.8	
		−3.3			108.9
$y^3P_0^\circ$	45722.5		$x^3F_2^\circ$	54992.9	
$x^3P_2^\circ$	51286.4		$w^3F_4^\circ$	57335.4	
		39.5			58.9
$x^3P_1^\circ$	51246.9		$w^3F_3^\circ$	57276.5	
		70.1			55.7
$x^3P_0^\circ$	51176.8		$w^3F_2^\circ$	57220.8	
$z^3D_3^\circ$	38911.4		$z^3G_5^\circ$	36211.9	
		180.7			177.9
$z^3D_2^\circ$	38730.7		$z^3G_4^\circ$	36034.0	
		133.6			136.3
$z^3D_1^\circ$	38597.1		$z^3G_3^\circ$	35897.7	
$y^3D_3^\circ$	46174.2		$y^3G_5^\circ$	46985.7	
		65.2			80.9
$y^3D_2^\circ$	46109.0		$y^3G_4^\circ$	46904.8	
		31.9			58.1
$y^3D_1^\circ$	46077.1		$y^3G_3^\circ$	46846.7	
$x^3D_3^\circ$	50264.4		$x^3G_5^\circ$	47055.1	
		80.3			0.4
$x^3D_2^\circ$	50184.1		$x^3G_4^\circ$	47054.7	
		78.5			6.4
$x^3D_1^\circ$	50105.6		$x^3G_3^\circ$	47048.3	
$w^3D_3^\circ$	55451.6		$w^3G_5^\circ$	48785.9	
		299.0			223.9
$w^3D_2^\circ$	55152.6		$w^3G_4^\circ$	48562.0	
		195.8			47.2
$w^3D_1^\circ$	54956.8		$w^3G_3^\circ$	48514.8	

TABLE 3.—*Odd terms of* Cr I—Continued

Term	ν	$\Delta\nu$	Term	ν	$\Delta\nu$
$v^3G_5^0$	54077.9		$r^3H_6^0$	63997.6	
		150.3			70.5
$v^3G_4^0$	53927.6		$r^3H_5^0$	63927.1	
		122.8			85.2
$v^3G_3^0$	53804.8		$r^3H_4^0$	63841.9	
$u^3G_5^0$	57088.1		$z^3I_7^0$	45954.0	
		54.7			−5.7
$u^3G_4^0$	57033.4		$z^3I_6^0$	45959.6	
		47.8			
$u^3G_3^0$	56985.6		$z^3I_5^0$		
$x^3H_6^0$	45348.6		$y^3I_7^0$	55798.9	
		−5.4			58.0
$x^3H_5^0$	45354.0		$y^3I_6^0$	55740.9	
		−4.5			54.6
$x^3H_4^0$	45358.5		$y^3I_5^0$	55686.3	
$y^3H_6^0$			$x^3I_7^0$	63028.3	
					198.2
$y^3H_5^0$	47298.8		$x^3I_6^0$	62830.1	
		157.2			193.7
$y^3H_4^0$	47141.6		$x^3I_5^0$	62636.4	
$x^3H_6^0$			$z^3J_8^0$	54498.0	
					93.1
$x^3H_5^0$	48136.3		$z^3J_7^0$	54404.9	
		93.8			88.2
$x^3H_4^0$	48042.5		$z^3J_6^0$	54316.7	
$w^3H_6^0$	48445.0		$z^5S_2^0$	43124.9	
		134.8			
$w^3H_5^0$	48310.2		$x'^5D_4^0$	46422.4	
		22.0			54.1
$w^3H_4^0$	48288.2		$x'^5D_3^0$	46368.3	
					19.0
$v^3H_6^0$			$x'^5D_2^0$	46349.3	
					51.1
$v^3H_5^0$	52965.4		$x'^5D_1^0$	46298.2	
		2.1			
$v^3H_4^0$	52963.3		$x'^5D_0^0$		
$u^3H_6^0$	54886.6		$u'^5F_5^0$		
		87.6			
$u^3H_5^0$	54799.0		$u'^5F_4^0$	48042.5	
		62.6			−209.5
$u^3H_4^0$	54736.4		$u'^5F_3^0$	48252.0	
					34.4
$t^3H_6^0$	54866.3		$u'^5F_2^0$	48217.6	
		−63.1			7.7
$t^3H_5^0$	54929.4		$u'^5F_1^0$	48209.9	
		118.6			
$t^3H_4^0$	54810.8		$z'^5H_7^0$	42386.9	
					135.0
$s^3H_6^0$	58775.2		$z'^5H_6^0$	42251.9	
		20.9			98.3
$s^3H_5^0$	58754.3		$z'^5H_5^0$	42153.6	
		26.1			73.8
$s^3H_4^0$	58728.2		$z'^5H_4^0$	42079.8	
					54.2
			$z'^5H_3^0$	42025.6	

The low and metastable terms of Cr I arise from the electron configurations d^4s^2, d^5s, and d^6. The terms for d^4s^2 and d^6 are similar in number and type and are characterized by wide fine structures, but those from d^6 will be inverted and relatively inconspicuous compared with those from d^4s^2, which are normal. On the other hand, the terms for d^5s are of narrow fine-structure and many of them exhibit total or partial inversion of their components. All of the septet and quintet terms arising from these 3 configurations have now been established; but of the triplet terms, required theoretically, not quite half have been found. No singlets have as yet been detected. These facts are summarized in table 4.

TABLE 4.—*Low and metastable terms of* Cr I

Electron configuration	Observed terms
$3d^4\ 4s^2$	a^5D, a^3H, b^3G, a^3F, a^3P
$3d^5\ 4s$	a^7S, a^5S, a^5G, a^3G, a^5F, b^3F, b^5D, a^3D, a^5P, b^3P, a^3I, l^3D
$3d^6$	c^5D

The identity of many of the triplet terms reported in this paper has been established by the excellent Zeeman effect observations made at the Mount Wilson Observatory by Mr. H. D. Babcock. It is a pleasure to acknowledge my indebtedness to him for placing his unpublished work at my disposal.

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USE OF 8-HYDROXYQUINOLINE IN DETERMINATIONS OF ALUMINUM, BERYLLIUM, AND MAGNESIUM

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ABSTRACT

The methods commonly used for precipitating aluminum by 8-hydroxyquinoline from an acetic-acid solution, buffered with ammonium acetate, do not sufficiently define the conditions requisite for complete precipitation. The present article describes a method in which aluminum is precipitated as the oxyquinolate from a solution which has been partially neutralized with ammonium hydroxide, using bromcresol purple as an indicator. Results obtained in the separation of aluminum from beryllium and magnesium, and in the separation of beryllium in the presence of aluminum, iron, titanium, and zirconium, by the described procedure, are given.

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I. INTRODUCTION

A study of the numerous procedures which have been recommended for the determination of aluminum and its separation from other elements by precipitating with 8-hydroxyquinoline reveals that, while conditions governing the precipitation from alkaline solutions have been satisfactorily established, those in which precipitation is effected from acid solutions have not been sufficiently defined. Procedures which recommend that precipitation be made from "faintly acid" or from "neutralized or weakly acid solution" are unsatisfactory, both because of the uncertainty in duplicating conditions for precipitation and the possibility of various interpretations by different analysts.

The recent investigations by H. R. Fleck and A. M. Ward [1] and by H. Gotô [2] have defined the limits within which certain elements are precipitated by 8-hydroxyquinoline. Experiments made by the latter show that aluminum is precipitated quantitatively between the pH values of 4.2 and 9.8. If aluminum is to be quantitatively separated as the oxyquinolate from an acid solution it is necessary therefore that precipitation be effected in a solution whose pH value is never less than 4.2 nor in excess of 7.0.

In the method to be described, aluminum is precipitated as the oxyquinolate from an acetic-acid solution, buffered with ammonium acetate, which has been neutralized with ammonium hydroxide to a pH of approximately 6.8, using bromcresol purple as an indicator. The aluminum oxyquinolate can be dried and weighed in that form, or it can be dissolved in hydrochloric acid and the solution thus obtained titrated with a standard solution of potassium bromate.

II. GENERAL CONSIDERATIONS

In any discussion of the use of 8-hydroxyquinoline as a precipitant, reference must be made to the extensive studies which have been carried out by R. Berg,[3] F. L. Hahn, and co-workers [4] and others.[5] From these it will be found that many elements are precipitated under essentially the same conditions and that direct separations are not always possible. The value of 8-hydroxyquinoline as a reagent in quantitative analytical chemistry lies principally, although not entirely, in its use after preliminary separations have removed interfering elements. Such separations may include precipitation with ammonium hydroxide, which serves to remove moderate amounts of elements such as magnesium, zinc, manganese, nickel, cobalt, tungsten, and molybdenum; electrolysis with a mercury cathode, which removes elements such as iron, chromium, nickel, cobalt, copper, zinc, tin, and molybdenum; precipitation with cupferron, which precipitates elements such as iron, titanium, zirconium, tin, columbium, tantalum, and others; or the separation of aluminum based on its solubility in sodium hydroxide.

Direct separation of aluminum by precipitating in an acid solution with 8-hydroxyquinoline is accomplished when dealing with solutions containing only aluminum, or aluminum in the presence of beryllium, magnesium, or other elements that are not precipitated in an acid solution, such as lead, the alkaline earth metals, and the alkalies.

The determination of aluminum oxide for the purpose of classifying commercial feldspar presents an almost ideal case in which a precipitation with 8-hydroxyquinoline from an acid solution is most advantageous. In this particular instance, the elements that are precipitated with the aluminum, such as iron, titanium, and zirconium, are generally present in such small quantities that their effect can be disregarded in commercial analyses. If these elements have been determined individually, corrections for their presence can be made.

The determination of beryllium in ores and metallurgical products frequently requires a separation of that element from aluminum,

[1] Analyst, **58**, 388 (1933).
[2] J. Chem. Soc. Japan **54**, 725 (1933).
[3] R. Berg, Z. anal. Chem. **70**, 341 (1927); **71**, 23, 171, 321, 369 (1927); **72**, 177 (1927); **76**, 191 (1929); **81**, 1 (1930).
[4] F. L. Hahn, et al., Z. anal. Chem. **71**, 122, 225 (1927).
[5] See also Organic Reagents for Metals, p. 41. (Hopkins and Williams, Ltd., London, 1933.)

with which it is often associated, as well as from certain other elements. For this purpose, precipitation of aluminum from an acid solution by 8-hydroxyquinoline completely separates that element from beryllium, which may then be determined in the filtrate by precipitating with ammonium hydroxide and igniting the precipitate to the oxide.[6] In such cases, a preliminary precipitation of the aluminum and beryllium with ammonium hydroxide is desirable to separate them from such elements as manganese, calcium, barium, strontium, and magnesium, which would subsequently interfere in the determination of beryllium if the latter is to be precipitated with ammonium hydroxide in the presence of 8-hydroxyquinoline.

In the analysis of alloys, the removal of such common alloying elements as copper, tin, iron, zinc, and nickel by electrolysis with a mercury cathode leaves a solution containing aluminum, and magnesium, if the latter be present. Other elements, such as titanium, zirconium, vanadium, and uranium, which are not removed by electrolysis, must be removed, if present, by other procedures before attempting the precipitation of aluminum. In this, and similar cases requiring a separation of aluminum from magnesium, precipitation from an acid solution by 8-hydroxyquinoline offers a rapid method for the direct separation and determination of aluminum.

III. EXPERIMENTAL WORK

Aluminum can be precipitated by 8-hydroxyquinoline from acid solution under two sets of conditions. In the one, as applied to the analysis of feldspar, the addition of a small amount of tartaric acid serves to prevent the formation of precipitates during the partial neutralization with ammonium hydroxide, and the aluminum is precipitated by a rapid addition of the reagent. In the other, with no tartaric acid, the precipitate that is formed by partial neutralization is either dissolved or converted to the oxyquinolate during the slow addition of the reagent. In the latter modification, the ability of 8-hydroxyquinoline to convert an insoluble compound to the oxyquinolate is of interest. R. Berg[7] states that even the difficultly soluble nickel glyoxime and the copper compound of α-benzoinoxime are converted into their respective oxyquinolates by treatment with 8-hydroxyquinoline.

1. DETERMINATION OF ALUMINUM

The determination of aluminum by precipitating with 8-hydroxyquinoline, although accomplishing a quantitative separation of that element, yields results that tend to be too high, regardless of whether the precipitate be dried and weighed as the anhydrous aluminum oxyquinolate or whether it be titrated, after solution in hydrochloric acid, with a standard solution of potassium bromate. The results given in table 1 were obtained by precipitating aluminum from an acid solution containing no other elements precipitable by 8-hydroxyquinoline. The aluminum in these precipitates was determined either by drying the precipitate at 140° C,[8] by titration of the dried precipitate after solution in hydrochloric acid, or by titration of

[6] I. M. Kolthoff and E. B. Sandell, J. Am. Chem. Soc. **50**, 1900 (1928). M. Niessner, Z. anal. Chem. **76**, 135 (1929).

[7] J. prakt. Chem. **115**, 182 (1927).

[8] The dried aluminum oxyquinolate is moderately hygroscopic and should be weighed without undue exposure to the atmosphere.

solutions of undried precipitates. A study of the results shows that, if amounts of aluminum not exceeding approximately 50 mg are involved, satisfactory determinations can be obtained by weighing the dried aluminum oxyquinolate. If aluminum is to be determined by titration the amount involved should not greatly exceed 25 mg, if correct results are to be expected. With larger amounts of aluminum, positive errors become noticeable regardless of whether the precipitate is dried and weighed, or whether it is titrated, after solution in hydrochloric acid, with potassium bromate. There appears to be a positive error in the determination of aluminum, resulting from probable retention of the reagent by the precipitate,[9] which is reflected more strongly in the volumetric procedure than in the gravimetric. This supposition was verified by the following experiments.

In two experiments, solutions containing 0.1890 g of aluminum oxide (0.1000 g of Al) were precipitated by the recommended procedure A and the aluminum oxyquinolate was decomposed in a platinum dish with sulphuric, nitric, and perchloric acids. Following the removal of platinum by precipitation with hydrogen sulphide, the aluminum was precipitated with ammonium hydroxide, filtered, washed, and ignited. The aluminum oxide obtained, corrected for silica and blanks, weighed 0.1890 and 0.1891 g.

TABLE 1.—*Results obtained in the determination of aluminum*

Experiment	Aluminum present [1]	Aluminum found						Remarks
		Drying at 140° C	Error	Titration (dry) precipitate	Error	Titration (wet) precipitate	Error	
	g	g	g	g	g	g	g	
1	0.0050					0.0051	+0.0001	*Procedure* B.—Precipitation in a volume of 125 ml containing 0.2 g tartaric acid and 4 g of ammonium acetate.
2	.0051					.0050	−.0001	
3	.0051					.0051	.0000	
4	.0101					.0102	+.0001	
5	.0253					.0253	.0000	
6	.0304					.0304	.0000	
7	.0248	0.0249	+0.0001	0.0250	+0.0002	.0249	+.0001	*Procedure* B.—Precipitation in a volume of 200 ml containing 1 g of tartaric acid and 4 g of ammonium acetate.
8	.0496	.0497	+.0001	.0501	+.0005	.0501	+.0005	
9	.0500	.0500	.0000	.0504	+.0004	.0505	+.0005	
10	.0500	.0502	+.0002	.0504	+.0004			*Procedure* A.—Precipitation in a volume of 200 ml containing 4 g of ammonium acetate.
11	.0500	.0503	+.0003	.0513	+.0013	.0514	+.0014	
12	.1000	.1005	+.0005					
13	.1000	.1003	+.0003	.1024	+.0024	.1028	+.0028	

[1] Solution prepared by dissolving metallic aluminum (99.97₅ percent of Al) in hydrochloric acid and standardized by precipitating with ammonium hydroxide and igniting to oxide, with final correction for silica.

With amounts of aluminum exceeding 50 mg, the following procedure is recommended. Dissolve the oxyquinolate in an excess of dilute sulphuric acid, evaporate to fumes of that acid and while fuming add successive small portions, 1 to 2 ml, of nitric acid (sp gr 1.50) to destroy the bulk of the organic matter. Cool the solution slightly, add one-third of its volume of perchloric acid (60 to 70 percent), and continue heating until the solution is colorless. Cool,

[9] F. L. Hahn, Z. anal. Chem. 86, 154 (1931).

dilute with water and heat to dissolve the anhydrous aluminum sulphate. Precipitate the aluminum with ammonium hydroxide, filter, wash, and ignite to oxide in the customary manner. Results must be corrected by blank determinations obtained by carrying similar known amounts of pure aluminum through all steps of the process involved in the destruction of organic matter, and for silica if the operations have been conducted in glass apparatus.

2. DETERMINATION OF ALUMINUM OXIDE IN FELDSPAR

The determination of aluminum oxide in feldspar, after removal of silica, presents a case which involves the separation of aluminum from the alkalies, and probably small amounts of calcium, barium, and magnesium. Iron, titanium, zirconium, and other elements are, in general, present in such small quantities as to make their prior removal unnecessary in ordinary work. Under such circumstances rapid routine determinations of alumina can be made by precipitating the aluminum from solutions representing 0.1 g of feldspar. Such solutions may be obtained from samples in which silica has been determined, or from individual portions of the feldspar which have been decomposed by hydrofluoric and sulphuric acids. In the latter case, it is essential that all hydrofluoric acid be expelled from the solution before attempting the precipitation of aluminum.

Results obtained in the analysis of feldspar by titrating the aluminum oxyquinolate, after solution in hydrochloric acid, with 0.1 *N* potassium bromate are given in table 2.

TABLE 2.—*Determination of aluminum oxide in feldspar*

Experiment	Al_2O_3			Sample
	Present [1]	Found	Difference	
	Percent	*Percent*	*Percent*	
1	18.03	18.01	−0.02	National Bureau of Standards Standard Sample 70.
2	18.03	18.06	+.03	Do.
3	18.03	18.02	−.01	Do.
4	19.06	19.10	+.04	Do.
5	19.06	19.11	+.05	Do.
6	19.06	19.14	+.08	Do.
7	15.33	15.34	+.01	
8	15.33	15.33	.00	
9	18.75	18.75	.00	
10	18.75	18.72	−.03	
11	14.30	14.40	+.10	
12	14.30	14.37	+.07	
13	21.25	21.09	−.16	
14	21.25	21.15	−.10	
15	21.25	21.12	−.13	

[1] Results given for experiments 7 to 15 are values reported by the analyst for a producer of commercial feldspar who used the standard method (double dehydration for silica and double precipitation with ammonium hydroxide), and who estimates that the values are accurate to ± 0.2 percent. The results for experiments 13 to 15 may be high because of the presence of an appreciable amount of barium in the sample.

3. SEPARATION AND DETERMINATION OF BERYLLIUM AND ALUMINUM

The precipitation of aluminum from acid solution by 8-hydroxyquinoline is of special importance because of the separation from beryllium that it accomplishes. Aluminum and beryllium are frequently associated with elements that either interfere in the deter-

mination of aluminum, or in the determination of beryllium when the latter is precipitated by ammonium hydroxide in the presence of 8-hydroxyquinoline. When such elements are present preliminary separations effecting their removal are necessary before attempting a precipitation of the aluminum. For this purpose, precipitation with hydrogen sulphide is required if elements such as copper, lead, bismuth, or other elements that form acid-insoluble sulphides are present. The removal of elements such as manganese, magnesium, the alkaline earth metals, and moderate amounts of nickel, cobalt, and zinc, is accomplished by precipitating with ammonium hydroxide, whereas precipitating with an excess of sodium hydroxide serves to separate aluminum and beryllium from iron, titanium, zirconium, and other elements whose hydroxides are insoluble in an excess of alkali.

(a) DETERMINATION OF ALUMINUM IN THE PRESENCE OF BERYLLIUM

Results obtained by precipitating aluminum oxyquinolate in acid solution, in the presence of beryllium, by procedure A, and drying the precipitate at 140° C are given in table 3. Although satisfactory separations are effected, the results are high because of retention of the reagent by the precipitate. The dried precipitates were dissolved by treatment with suphuric, nitric, and perchloric acids, and examined for beryllium by treating with sodium hydroxide and quinalizarin as recommended by H. Fischer.[10]

TABLE 3.—*Determination of aluminum in the presence of beryllium*

Experiment	Aluminum taken [1]	Beryllium taken	Aluminum found	Error	Beryllium contained in aluminum precipitate
	g	g	g	g	mg
1	0.1000	0.1083	0.1006	+0.0006	0.1
2	.1000	.0011	.1004	+.0004	.0
3	.0500	.1083	.0503	+.0003	.1
4	.0100	.1083	.0101	+.0001	.0

[1] See footnote to table 1.

(b) DETERMINATION OF BERYLLIUM IN THE PRESENCE OF ALUMINUM, IRON, TITANIUM, AND ZIRCONIUM

Results obtained in the determination of beryllium, after its separation from aluminum, iron, titanium, and zirconium by precipitating the latter in acid solution with 8-hydroxyquinoline by the recommended procedure, are given in table 4. In these experiments, double precipitations with 8-hydroxyquinoline were made to recover the small amount of beryllium retained by the first precipitate, and the combined filtrates were evaporated and treated with sulphuric, nitric, and perchloric acids to destroy the excess reagent before precipitating the beryllium as the hydroxide. Subsequent experiments showed that it is not necessary to remove the excess of 8-hydroxyquinoline from solution, since it does not interfere with the complete precipitation of beryllium by ammonium hydroxide if the solution is allowed to cool before it is filtered.

[10] Z. anal. Chem. 73, 54 (1928).

TABLE 4.—*Results obtained in the determination of beryllium after its separation from aluminum, iron, titanium, and zirconium*

Experiment	BeO taken [1]	BeO found			Error	Other elements present
		First separation	Second separation	Total		
	g	g	g	g	g	g
1	0.3004	0.2996	0.0006	0.3002	−0.0002	0.10 Al_2O_3
2	.1502	.1497	.0005	.1502	.0000	.01 Fe_2O_3
3	.0150	.0150	.0002	.0152	+.0002	.005 TiO_2
4	.0015	.0014	.0000	.0014	−.0001	.005 ZrO_2

[1] Solution prepared from beryllium carbonate, free from aluminum, and treated to remove elements whose sulphides are insoluble in acid. The solution, after 3 precipitations with ammonium hydroxide to insure removal of any magnesium, was standardized by precipitating with ammonium hydroxide and igniting to oxide, with final correction for silica.

Incomplete precipitation was observed in a few cases in the separation of beryllium as the hydroxide by precipitating with ammonium hydroxide from hot solutions. To recover any beryllium that may have escaped precipitation the filtrates were allowed to cool, treated with a few drops of ammonium hydroxide and allowed to stand for 24 hours—a precaution also recommended by M. Frommes.[11]

The total beryllium oxide recovered in each experiment was examined for contaminating elements and found to contain less than 0.1 mg of aluminum oxide, a trace of ferric oxide, and no titanium or zirconium oxides. Solutions of the final oxyquinolate precipitate, after treatment with sulphuric, nitric, and perchloric acids to destroy organic matter, were precipitated with an excess of sodium hydroxide, and filtered. The filtrate, when treated with quinalizarin, showed the oxyquinolate precipitate to be free from beryllium.

4. DETERMINATION OF ALUMINUM IN THE PRESENCE OF MAGNESIUM

The results given in table 5 were obtained by precipitating aluminum in the presence of magnesium, by the recommended procedures, and drying the aluminum oxyquinolate at 140° C. The values obtained illustrate again the tendency of the method to yield results that are too high because of retention of the reagent by the precipitate.

TABLE 5.—*Determination of aluminum in the presence of magnesium*

Experiment	Aluminum taken [1]	Magnesium taken	Aluminum found	Error	Precipitation by procedure—
	g	g	g	g	
1	0.0010	0.1000	0.0010	+0.0000	B
2	.1000	.0500	.1002	+.0002	A
3	.1000	.0500	.1005	+.0005	A
4	.1000	.1000	.1002	+.0002	A
5	.1000	.1000	.1005	+.0005	A
6	.1000	.1000	.1006	+.0006	B
7	.1000	.1000	.1005	+.0005	A

[1] See footnote to table 1.

[11] Z. anal. Chem. 93, 287 (1933).

The aluminum oxyquinolate obtained in experiments 1 to 5 was decomposed as described in section III, 1. Determination of aluminum, and the aluminum, in each, twice precipitated with ammonium hydroxide. The combined filtrates, when evaporated to a small volume and treated with diammonium phosphate, failed to disclose the presence of magnesium. Under conditions of the tests 0.2 mg of magnesium would have been detected.

IV. RECOMMENDED PROCEDURES

1. PROCEDURE A (FOR USE IN PRESENCE OF BERYLLIUM)

To the acid solution containing not more than 0.1 g of aluminum and 10 ml of hydrochloric acid in a volume of 200 ml, add 15 ml of a solution prepared by dissolving 30 g of ammonium acetate in 75 ml of water, and 8 to 10 drops of a 0.04-percent solution of bromcresol purple. Add diluted ammonium hydroxide (1+1) [12] until the indicator becomes a distinct purple. While stirring, add slowly from a burette an acetic-acid solution of 8-hydroxyquinoline in 15 to 25 percent excess of the amount necessary to precipitate the aluminum. Stir occasionally as the solution and precipitate are heated to boiling and boil gently for 1 minute. Allow to cool to 60° C. Filter the precipitate (using moderate suction) through a 35-ml fritted-glass crucible of fine porosity, such as a 1bG4 Jena-glass filtering crucible. Wash the precipitate with 100 ml of cool water and determine the aluminum by either of the methods given under procedure B.

2. PROCEDURE B (FOR USE IN ABSENCE OF BERYLLIUM)

To the acid solution containing not more than 0.1 g of aluminum and 10 ml of hydrochloric acid in a volume of 200 ml, add tartaric acid in an amount equal to 5 times the weight of aluminum that is to be precipitated. Add 15 ml of a solution prepared by dissolving 30 g of ammonium acetate in 75 ml of water, and 8 to 10 drops of bromcresol purple solution. Partially neutralize the solution by adding diluted ammonium hydroxide (1+1) until a distinct purple color appears. While stirring, add rapidly an acetic-acid solution of 8-hydroxyquinoline in 15 to 25 percent excess of the amount necessary to precipitate the aluminum. Complete the separation by heating, filtering, and washing the precipitate as directed in procedure A.

The treatment of the precipitate to determine the aluminum may be carried out either gravimetrically or volumetrically. In gravimetric determinations, involving as much as 0.1 g of aluminum, dry the precipitate 3 hours at 135° C and weigh as $Al(C_9H_6ON)_3$, which contains 5.87 percent of aluminum or 11.10 percent of aluminum oxide.

If aluminum is to be determined by the volumetric procedure, place the crucible and its contents in a 600-ml beaker, add 200 ml of diluted hydrochloric acid (1+4) and heat gently until the precipitate has dissolved. Remove the crucible and rinse the adhering solution back into the beaker. Recover the solution retained in the glass frit by replacing the crucible on the filtration apparatus and washing it with warm dilute hydrochloric acid (1+9). Dilute the acid solution to 400 ml and cool to room temperature (20° C±3°).

[12] Made by diluting 1 volume of ammonium hydroxide (sp gr 0.90) with 1 volume of water. When no dilution is specified the use of the concentrated reagent is intended.

Add a solution of standard potassium bromate-potassium bromide [13] in moderate excess (about 2 to 3 ml), as determined by test,[14] or by calculation if the approximate amount of aluminum is known. Stir and let stand for 30 to 60 seconds to insure complete bromination. Add 15 ml of a 20-percent solution of potassium iodide, stir thoroughly to make sure that the reaction between the bromine and the iodide is complete, and then titrate with a 0.1 *N* solution of sodium thiosulphate until the color of the solution becomes a faint brownish yellow.[15] Add 4 ml of starch solution and titrate until the blue color disappears.

Subtract from the volume of the potassium bromate-bromide added the volume of potassium bromate-bromide solution which is equivalent to the volume of sodium-thiosulphate solution that is required. Multiply the difference, representing the volume of potassium bromate-bromide consumed in reacting with the 8-hydroxyquinoline, by the titer of this solution to obtain the amount of aluminum.

The solutions that are required for the determination of aluminum are as follows:

Potassium bromate-bromide solution (1.0 N).[16]—Dissolve 27.835 g of potassium bromate and 100 g of potassium bromide in 600 ml of water and dilute to exactly 1 liter. The potassium bromate-bromide solution is conveniently standardized by determining the ratio between it and a solution of sodium thiosulphate which has been standardized against an iodine solution. This ratio is obtained as follows: To 200 ml of cool water containing 4 g of potassium iodide, add 4 ml of *N* bromate (or 8 ml of 0.5 *N*, 16 ml of 0.25 *N*, or 40 ml of 0.1 *N*, if such solutions are preferred). Add quickly, while stirring, 40 ml of diluted hydrochloric acid (1+1) and titrate with thiosulphate until the solution is nearly colorless. Add 4 ml of starch solution and continue the titration until the blue color disappears.

In treating oxyquinolates with potassium bromate, 4 gram-atoms of bromine are required for each quinolate radical. Consequently, 12 gram-atoms of bromine represent 1 gram-atom of aluminum, and 1 ml of an exactly normal solution of potassium bromate-bromide should equal

$$\frac{26.97}{12}\times\frac{1}{1000}=0.0022475 \text{ g of aluminum.}$$

The titer of the bromate solution is then obtained as follows:

$$\text{Normality factor of the thiosulphate solution}\times\frac{\text{ml of thiosulphate solution}}{\text{ml of bromate solution}}=\text{normality factor of the bromate solution.}$$

[13] The bromate solution used in the titration should be of such strength that a reasonable volume is consumed in performing the titration. Suitable strengths vary from 0.1 *N*, for amounts of aluminum up to 10 mg, to *N* for amounts such as 50 to 100 mg.

[14] Add 1 drop of the solution to a mixture of 1 drop of potassium-iodide solution and 1 drop of starch solution on a spot plate. If the mixture turns blue, stir the solution containing the aluminum 1 minute and repeat the test. If the blue color does not again appear, more bromate solution must be added and the test repeated. Berg (Z. anal. Chem. **71,** 31 (1927)) recommends the use of a few drops of a 1-percent aqueous solution of indigo carmine, while Hahn and Vieweg (Z. anal. Chem. **71,** 124 (1927)) use a diazobenzenesulphonic-acid paper instead of iodide and starch.

[15] In titrating the liberated iodine, the addition of the thiosulphate is continued until the solution is a pale brownish yellow. Care in distinguishing between this color and the yellow color due to the brominated 8-hydroxyquinoline is necessary.

[16] Solutions of 0.5, 0.25, and 0.1 *N* are prepared by dissolving potassium bromate and potassium bromide in similar proportions.

This normality factor×0.0022475=g of Al per ml of the bromate solution.

Sodium-thiosulphate solution (0.1 N).—Dissolve 25 g of sodium thiosulphate ($Na_2S_2O_3.5H_2O$) in 200 ml of recently distilled water and dilute to 1 liter. Standardize this solution against a 0.1 *N* solution of resublimed iodine which has been standardized against pure arsenious oxide.

8-Hydroxyquinoline solution (2.5 percent).—Treat 12.5 g of 8-hydroxyquinoline with 25 ml of glacial acetic acid and warm gently to effect solution. Pour the resulting solution into 450 ml of water at 60° C. Cool, filter if necessary, and dilute to 500 ml.

Potassium-iodide solution (20 percent).—Dissolve 25 g of potassium iodide in 100 ml of water.

Starch solution.—Dissolve 5 g of soluble starch and 2.5 g of salicylic acid in 1 liter of water.

Bromcresol-purple solution (0.04 percent).—Triturate 0.1 g of the dry indicator with 18.5 ml of 0.01 *N* sodium hydroxide and dilute the resulting solution with water to 250 ml.

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A THIN CELL FOR USE IN DETERMINING THE REFRACTIVE INDICES OF CRYSTAL GRAINS

By Charles Proffer Saylor

ABSTRACT

The use of those immersion methods for determining refractive index in which a regulation of temperature is employed has been seriously limited by the impossibility of obtaining interference figures. A thin cell is described which overcomes this obstacle, so that it is possible to know the exact orientation of the crystal grains which are chosen for identification.

A distinct impediment in applying the double-variation method of Emmons [1] for determining refractive indices has been the impossibility of obtaining conoscopic interference figures. As it is only in special cases, therefore, that the optical orientation of a crystal grain can be accurately known, the peculiar advantages of the method are almost lost. Emmons endeavors to remedy this situation in a later publication,[2] in which he describes an application of the universal stage to the problem, but this method is cumbersome and slow, and a large proportion of particles are too small to be studied with it.[3]

Emmons mounts the preparation upon a cell with glass windows, between which water of controlled temperature is circulated. The temperature of the liquid mounting of the crystal fragments quickly becomes almost the same as that of the water. The refractive index of the liquid is modified accordingly and can be made to match an index of the immersed crystal fragments. But this cell is so thick that the preparation is raised above the region traversed by the more oblique rays. Consequently, satisfactory interference figures are impossible. To avoid this difficulty, the writer, three years ago, constructed a cell of different form. It has been successful, and during three years of use no reason has appeared for modifying the design shown in figure 1.

Three pieces of brass A, B, and C, which are 0.5, 0.9, and 0.2 mm thick, respectively, were cut along the full lines with a jeweler's jig saw. Two holes were drilled in A, as shown. From B, clamped upon a plane surface, half the thickness of the parts indicated by stippling was removed with a chisel, and, in the same manner but from the reverse side, half the thickness was removed from those parts indicated by crosshatching. The bottom of A, the top and bottom of B, and the top of C were thinly coated with solder; the

[1] R. C. Emmons, Am. Mineral. **13**, 504 (1928); **14**, 414 (1929).

[2] A. N. Winchell, The Microscopic Characters of Artificial Inorganic Solid Substances or Artificial Minerals, (John Wiley & Sons, Inc., 1931). Chapter VIII, on the Universal Stage, was written by Emmons.

[3] These difficulties are clearly set forth in a review of Winchell's book by G. Tunell and G. W. Morey, J. Am. Chem. Soc. **54**, 2574-7 (1932).

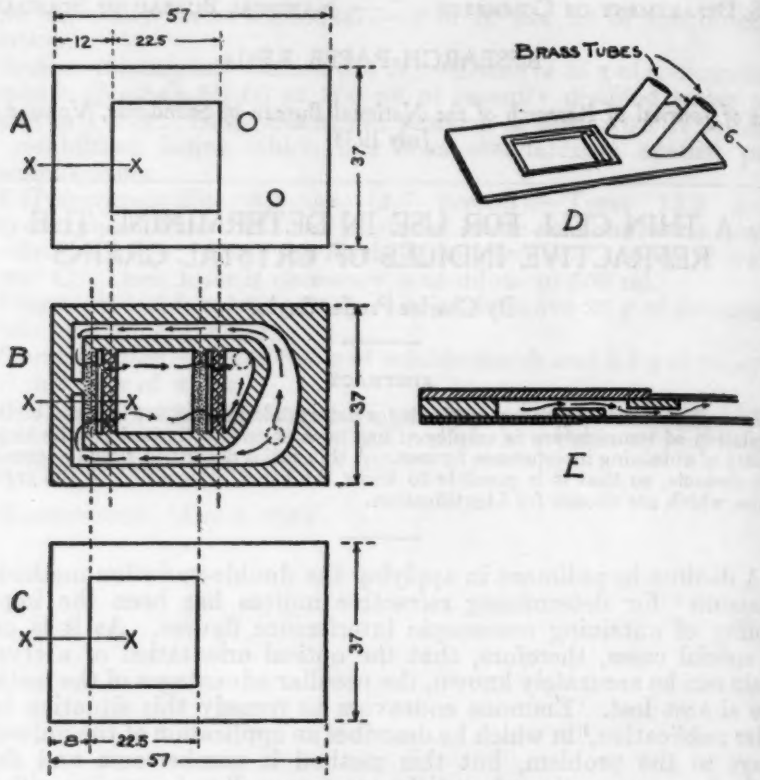

FIGURE 1.—*Details of the cell.*

A, B, and C are three-fifths their actual size. E, taken along the line xx, is four times the scale of A, B, and C. All dimensions are given in millimeters.

three pieces were superimposed and sweated together. The solder which extruded around the edges of the brass plates and the window was removed, and the edges were smoothed. The two short pieces of brass tubing indicated in D, each with a bevelled end, were soldered over the holes in A. Square cover glasses (no. 2; 22 mm) were cemented in the recesses [4] which were provided, top and bottom, by the shapes of the pieces A, B, and C. A perspective drawing of the completed cell is shown in figure 1 (D), and in figure 1 (E) a section along the dotted line xx is shown. The metal parts are hatched.

The apparatus is satisfactorily durable despite the thinness of the cover glasses. Cementing along the four edges lends much strength, and the cover glasses have never been accidentally broken. In the completed cell the distance from the bottom of the lower cover glass to the top of the upper one is 1.35 mm. The thickness of the cell, therefore, is about the same as that of an average microscope slide, and it is used like one. There is no difficulty in obtaining interference figures or controlling the temperature with all desirable accuracy.

[4] Of various cements tried, only Schaar & Company's Cementyte D proved satisfactory. The others loosened when very hot water was circulated through the cell.

WASHINGTON, April 30, 1935.